

BOOK of ABSTRACTS

# ISMANAM

Roma, 2-6 July 2018

25<sup>TH</sup> INTERNATIONAL SYMPOSIUM ON METASTABLE,  
AMORPHOUS AND NANOSTRUCTURED MATERIALS





**PLENARY LECTURE**

Chair: K. Kelton

**Structure modulation and nanocrystallization of metallic glasses: how to tune mechanical properties**

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Metallic glasses are known for their outstanding mechanical strength but limited plasticity. Significant progress has been made in recent years in how to optimize processing conditions for bulk glass formation, net-shape forming and the microscopic mechanism of failure. However, the details of the correlation between atomic structure, defects and thermo-mechanical treatments utilized for structure modification and their impact on shear band nucleation and propagation for achieving macroscopic ductility are still not well-understood.

This talk attempts to shed light on structural (re)ordering, recovery and rejuvenation mechanisms, as well as nanocrystallization phenomena in different metallic glasses when they are subjected to different casting conditions, relaxation or thermoplastic net-shaping. The findings will be discussed with respect to short- and medium-range order modulation, defect generation and annihilation, and precipitation of secondary phases. The structural changes will be correlated with changes in plastic deformability and failure mechanisms, and the effectiveness of composition tuning and thermo-mechanical processing for plasticity improvement will be analyzed in order to derive design aspects and processing guidelines for property optimization of metallic glasses.

**Monday 2 July morning - 10:00/13:00**

Parallel Session 1  
**METALLIC GLASSES I**  
M. Atzon, Chair

**ID-99 (Invited)****Origin of fragility and the onset of cooperative dynamics in liquids***K. Kelton**Washington University*

For strong liquids the viscosity is Arrhenius over a wide temperature range, while fragile liquids are non-Arrhenius, having a temperature-dependent activation energy [1]. It appears that all liquids are Arrhenius at a sufficiently high temperature, but not clear why this changes with cooling. While fragility is also reflected in properties such as the entropy and specific heat, Poisson's ratio, and rate of structural evolution of the liquid, the origin of fragility remains unclear. Of fundamental interest, these questions also have practical relevance since fragility is widely believed in the metallic glass community to be related to glass formability [2,3].

The origin of fragility and the microscopic mechanisms responsible for the onset of a non-Arrhenius temperature dependence of the viscosity will be explored in this talk. Experimental and molecular dynamics studies will demonstrate that fragility is related to the character of the interatomic potential [4], providing a fundamental reason for its emergence in the dynamical, structural, and mechanical properties of the liquid and glass. Molecular dynamics studies suggest that the onset of non-Arrhenius behavior in the viscosity with decreasing temperature is due to the onset of atomic cooperativity [5,6], also influenced by the character of the potential. The onset occurs at a materials characteristic temperature,  $T_A$ , that is generally 5 to 10% above the liquidus temperature. Recently obtained inelastic neutron scattering data from metallic liquids that support the MD results will be presented and discussed. Finally, it will be shown that the glass transition temperature can be accurately predicted by knowing  $T_A$  and the thermal expansion coefficient of the liquid.

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[2] R. Busch, E. Bakke, W. L. Johnson, Acta Materialia, 46, 4725 (1998)

[3] W. L. Johnson, J. H. Na, M. D. Demetriou, Nature Communications, 7, 10313 (2016)

[4] C. E. Pueblo, M. Sun and K. F. Kelton, Nature Materials, 16, 792 (2017).

[5] T. Iwashita, D. M. Nicholson and T. Egami, Physical Review Letters, 110, 205504 (2013)

[6] R. Soklaski, V. Tran, Z. Nussinov, K. F. Kelton, L. Yang, Philosophical Magazine, 96, 1212 (2016).

## ID-98

**Corrosion and impedance behavior of  $Zr_{42}Cu_{50}Ag_8$  bulk metallic glass in artificial physiological solutions**

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<sup>1</sup> NITK Surathkal

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Zr-based BMGs, is a promising possibility in biomedical applications due to absence of toxic elements and biocompatibility characteristics. The present paper deals corrosion and electrochemical impedance behaviour of newly developed  $Zr_{42}Cu_{50}Ag_8$  BMGs in various artificial physiological solutions such as artificial blood plasma (ABP), Hank's, artificial saliva (ASS), Ringers and phosphate buffered saline (PBS) solutions.

Potentiodynamic polarization and EIS studies were carried out to examine the passivation behaviour and susceptibility to localized corrosion. It was observed that the BMG showed good corrosion resistance in PBS and ASS solution with lower corrosion rate of 1.282 and 1.806 mpy respectively when compared to high corrosion rate of 2.321, 5.60 and 7.482 mpy in ABP, Hank's and Ringer's solution respectively. EIS tests were conducted with the help of potentiostat attached with frequency analyser. The whole cell was kept at a temperature of 37°C according to ASTM standard. The polarization resistance ( $R_p$ ) was observed about 48633, 95325, 135093, 39221 and 45006 ohms.cm<sup>2</sup> in the solutions of Hank's, artificial saliva, phosphate buffered saline, artificial blood plasma and Ringers respectively. The lowest passivation tendency of newly developed BMGs was found in artificial blood plasma solution due to presence of high aggressive of chlorides and others ions as compared to other physiological environment.

## ID-133

**Nitrogen plasma immersion ion implantation treatment enhances the corrosion resistance, blood coagulation, and cell response of Zr-based bulk metallic glass for implant applications**

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This study investigated the application of nitrogen plasma immersion ion implantation (NPIII) for the surface modification of Zr-based bulk metallic glass (BMG),  $Zr_{62.5}Cu_{22.5}Fe_5Al_{10}$ , without altering the crystalline structure of Zr-based BMG. This treatment produced a dense, protective layer (thickness of approximately 15 nm) on the surface of Zr-based BMG. This layer comprised oxides as well as nitrides, most of which were  $ZrO_2$ ,  $Zr(N,O)$ , and  $ZrN$ . NPIII treatment did not significantly alter the surface morphology, roughness, and wettability of the Zr-based BMG. The NPIII treatment enhanced the resistance of Zr-based BMG to corrosion, especially pitting corrosion, in artificial saliva and simulated blood plasma solutions. Protein adsorption response analysis indicated that the nitride-containing oxide layer produced by NPIII treatment enhanced the adsorption of albumin and fibronectin. Blood coagulation analysis indicated that the nitride-containing oxide layer enhanced the platelet adhesion and activation. In addition, NPIII-treated Zr-based BMG was shown to promote the adhesion, proliferation, and differentiation of human bone marrow mesenchymal stem cells. Our results demonstrate that the unique amorphous structure of Zr-based BMG can be maintained after NPIII surface modification. Our results also indicate the potential of NPIII-treated Zr-based BMG as a material for hard tissue implants with enhanced corrosion resistance and biological responses.

## ID-152

**Characterization of oxide layers developed on ZrCuAl-based bulk metallic glasses during gaseous thermochemical treatment**

*S. Haratian, M. Villa, F.B. Grumsen, T.L. Christiansen, M.A.J. Somers*

*Technical University of Denmark (DTU)*

The current study addresses an investigation of low-temperature oxidizing treatment ( $<T_g$ ) of ZrCuAl-based BMGs, which have been monitored by thermogravimetry. The thermochemical treatment was applied in two different gaseous atmospheric conditions providing low and high oxygen partial pressures. The microstructural evolution and surface morphology of the oxidation zone developing during the treatment of ZrCuAl-based BMGs were investigated utilizing X-ray diffraction and advanced electron microscopy techniques. The oxygen-containing case formed in the metallic glassy substrate was further investigated with in-situ ion beam channeling. The results demonstrate that after conducting the oxidizing treatment in the atmosphere containing high oxygen partial pressure, an outer oxidation layer and an inner oxide zone develop. In the gas with a low oxygen partial pressure only the inner oxidation zone results. Interestingly, four oxide regions with different chemical composition, which mainly consist of  $ZrO_2$  (with two different lattice structures; tetragonal and monoclinic) and  $Al_2O_3$  are present in the inner layer where the oxygen is distributed through the substrate. Furthermore, the outer oxide layer is enriched in copper which has diffused out of the BMG. Cracks have developed adjacent to the surface, which is ascribed to the stresses resulting from oxide formation in the inner oxidation zone. Some of the cracks are filled out with copper. This phenomenon was also observed in Ag-containing BMG, where both copper and silver enrich at the surface.



**ID-163**

## Atomic structure and devitrification of Ca-based metallic glasses

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With increasing aging population and improvement of living standards, there is rising demand of new biomaterials. Specific clinical cases require sometimes only temporary implant materials where support is needed only for the healing process after which it dissolute in human body. In this view, biodegradable or bioresorbable materials based on Ca, Mg and Zn elements are the optimal choice as those materials consists of elements pre-existing in the human body which has an inherent tolerance to them.

Low density metallic glasses were produced by rapid solidification melt-spinning process. The re-ported glasses are consisting solely of biocompatible elements with the view to its potential use as bioresorbable alloy for orthopaedic applications. Density, elastic modulus, hydrogen storage capacity, thermal properties of selected metallic glasses, such as the glass transition, crystallization and melting temperatures, as well as heats of crystallization and melting will be presented. The full devitrification process of selected biodegradable amorphous alloys up to its melt will be shown for the first time.

**Monday 2 July morning - 11:30/13:00**

Parallel Session 2  
**NANOSTRUCTURED MATERIALS I**  
Chair: E. Tamburri

**ID-423 (Invited)****Stability and deformation behavior of nanocrystalline high entropy alloys***B.S. Murty**IIT Madras*

High entropy alloys (HEAs) are a new class of multi-component equiatomic (or near equiatomic) alloys, which are expected to form simple solid solutions due to their high configurational entropy. However, there are a number of cases where these HEAs have shown more than one phase and in some cases the presence of intermetallics too, though these intermetallics are not binary in nature. Prediction of the phase formation in HEAs is a major challenge in this field. Phase diagram calculations using Calphad approach indicate that many of the HEAs show the presence of intermetallics at low temperatures. Stability of the microstructure at higher temperatures is essential for use of these HEAs for elevated temperature applications. Understanding the stability the phases in these systems is a major challenge due to possible sluggish diffusivity in these alloys making it difficult to understand whether the phases obtained are thermodynamically stable or kinetically stabilized.

The present paper highlights Calphad calculations in a number of HEA systems for predicting the phase formation at various temperatures and experimental efforts in validating these phase diagrams. Efforts were also made in the present work to measure the diffusivities in some of the HEA compositions both through interdiffusion studies and tracer diffusion studies to get a better understanding on the stability of the phases in the HEA systems. The paper also brings out the work carried out in the research group of the author for identifying the processing window and understanding the deformation behavior in some of these HEAs.

**ID-100****Mechanical properties of nanostructured materials embedded with nanotwins**

*N.R. Tao, F.K. Yan, B.B. Zhang*

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Induction of high density nanotwins was used to strength metallic materials in recent years. In our work, nanostructured materials consisting of nanotwins and nanograins were prepared by using dynamic plastic deformation in various materials including copper and its alloys, as well as steels. These nanostructured materials exhibit a high strength, but with a very limited ductility. Subsequent thermal annealing makes nanograins recrystallize into micro-sized grains while most strain-induced nanotwins still survive with a reduced dislocation density, forming a mixed nanostructure consisting of nanotwins and recrystallized coarse grains. The nanotwins strengthen the materials and recrystallized coarse grains impart ductility during deformation, resulting in an enhanced combination of strength and ductility. In comparison with homogeneous nanostructured materials and “bimodal” structure, this kind of mixed nanostructured materials embedded with nanotwins exhibit advantages especially in mechanical properties. These results showed that tailoring microstructures is a potential approach to obtain advanced nanostructured materials.

**ID-128****Interface-modulated strengthening ability of nanoscale Cu/Au multilayers**

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Interfaces in materials can play an important role in determining mechanical performance of the materials through the complicated interaction between defects and interfaces. In metallic multilayers, interface barrier strength (IBS), which refers to the resistance for dislocations to cross an interface, is a key factor to determine the ultrahigh strength of nanoscale multilayers. Although several theoretical models have been proposed to describe strengthening mechanisms in multilayers and primary contributions to the IBS, the variation of interface properties caused by element interdiffusion at atomic scales and its influence on the IBS of the multilayers are still not well understood. In this talk, we will present experimental and theoretical investigations of the IBS of Cu/Au multilayers, emphasizing effects of interface properties and structures. The Cu/Au multilayers with individual layer thickness ranging from 25 to 250 nm were annealed at different temperatures to modulate Cu/Au interface properties. Experimental results from nanoindentation testing show that the Halletch slope in the relation between the strength and the individual layer thickness of the multilayers gradually decreases with increasing annealing temperature, indicating a decrease in the IBS. TEM and HRTEM characterization reveals that element interdiffusion between the Cu layer and the adjacent Au layer leads to a compositional gradient at the interface. A detailed analysis for effects of the compositional gradient on the resistance to dislocation crossing the interface was conducted. It is demonstrated that the interface structure of the Cu/Au multilayers has become the most important factor in governing the IBS.

## ID-174

**Enhancing the wettability of nano-scale Cu thin film on ZnO substrate by gas additives: A density-functional study***E. Choi, J. Yun, S.Z. Han**Computational materials research group, Korea Institute of Materials Science*

Metallic ultra-thin films have attracted much attention as a favorable candidate for flexible transparent conducting electrodes because of high conductivity and good flexibility of metals. However, the growth of metal nanoclusters results in less densification due to agglomeration, and it lead the low transmittance of metal films with nano-scale thickness. Much effort has been made to obtain the continuous metal ultra-thin films. For example, the wettability of metal films was improved by forming an alloy with different metals such as Aluminum or by introducing a surfactant layer [1,2]. In recent studies, ultra-thin continuous copper films having a thickness of approximately 2 nm were achieved by addition of oxygen and nitrogen [3,4]. However, the influence of the gas atom solution in copper film on the wetting behavior have not been clarified yet. Here, we prove that gas additives at the initial state of Cu deposition can suppress the growth of Cu islands on oxygen-terminated ZnO surface through the first-principle calculations. We perform the density functional calculations using the Vienna Ab-initio simulation package code (VASP) to obtain formation energies and electronic structures of Cu thin films on ZnO surface. Our calculations show that gas additives such as oxygen and nitrogen prefer to reside on the surface of Cu films and at the Cu/ZnO interface. We extract the spreading parameter (S) of Cu films with gas additives based on the DFT simulations. As a result, gas additives increase the spreading parameter of Cu when these atoms are located on the surface of Cu or at the Cu/ZnO interface. Analysis of the electronic structure of Cu with gas additives reveals that gas additives stabilize the Cu ions by lowering of non-bonding states of Cu at the surface and Cu/ZnO interface. Thus, gas additives such as oxygen and nitrogen can reduce the surface and interface energies of Cu films on ZnO, leading to the enhancement of the wettability of Cu films on ZnO substrate.

[1] D. Gu, C. Zhang, Y.-K. Wu and L. J. Guo, ACS Nano 8, 10343-10351 (2014).

[2] S. Schubert, J. Meiss, L. Müller-Meskamp and K. Leo, Adv. Energy Mater. 3, 438-443 (2013).

[3] C. Zhao, W. Wang, T.-S Bae, S.-G Lee, C. Mun, S. Lee, H. Yu, G.-H. Lee, M. Song and J. Yun, Nature commun. 6, 8830 (2015).

[4] C. Zhao, S. M. Kim, S.-G. Lee, T.-S. Bae, C. Mun, S. Lee, H. Yu, G.-H. Lee, H.-S. Lee, M. Song and J. Yun, Adv. Funct. Mater. 26, 4180-4191 (2016).

## ID-41

**Tribological and corrosion property of Fe-based metallic glass nanocomposite coatings synthesized by thermal spraying**

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Fe-based metallic glass composite coatings were developed by thermal spraying of multi-component Fe based amorphous alloy powders at varying spraying power onto the mild steel substrate. The thermodynamic parameters, viz. atomic size difference ( $\delta$ ), mixing enthalpy ( $\Delta H_{\text{mix}}$ ), mixing entropy ( $\Delta S_{\text{mix}}$ ), mismatch entropy (S), and PHSS, were calculated to predict the glass forming ability (GFA) of the present Fe-based alloy composition. The morphology, microstructure, and crystallinity in the plasma sprayed coatings were analyzed by SEM, XRD, TEM and DSC. The observed results revealed that the coatings exhibited relatively less porosity (4.2-5.4%) and high amount of retained amorphous phase (87-92%) with nanocrystalline  $\alpha$ -Fe and several types of iron borides embedded in the amorphous matrix. The mechanical (hardness, and reduced elastic modulus) and the tribological (coefficient of friction) properties of the coatings were examined using nanoindentation and nanoscratch techniques, respectively. The coatings with increasing thermal power exhibited higher nano-hardness and elastic modulus. Moreover, coatings deposited at different heat input showed similar steady state friction coefficient values (0.43-0.51) and lower penetration depth. Corrosion resistance of the coatings was examined via standard potentiodynamic polarization test using 3.5% NaCl solution open to air at 298 K. The results showed that the coatings exhibited better corrosion resistance than mild steel and galvanized steel.

**Monday 2 July morning - 11:30/13:15**

Parallel Session 3  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES I**  
Chair: A. Calka



**ID-382 (Invited)****Rapid solidification of AlSi<sub>10</sub>Mg + Cu mixed powders by single track laser melting and melt spinning**

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Additive Manufacturing (AM) technologies such as Selective Laser Melting (SLM) imply fast melting and solidification of layers of powders on a growing object of the same composition. Heat subtraction is strongly directional implying high spatial temperature gradient and fast growth rate.

The present industrial applications of SLM make use of atomized powders of conventional foundry alloys, especially in the case of light alloys based on Al, i. e. alloys of the Al-Si system. The mechanical properties of these materials cannot be improved significantly by means of conventional hardening processes. The most relevant contribution to hardening comes from the microstructure refinement due to rapid solidification [1]. New alloy formulation may improve the performance of SLM products, one route being the addition of hardening elements to the base alloy.

In this work, we present preliminary results on rapid solidification of mixed Al-Si<sub>10</sub>Mg and Cu powders performed both by single track laser melting and melt spinning. The comparison of microstructure and phase constitution of the samples provides a mean for interpreting the fast events occurring in SLM processing: melting, epitaxial growth, recalescence, precipitation [2]. Nano-indentation mapping on sample cross-section gives a clear picture of the effects of rapid solidification, precipitation and particle coarsening indicating the need for dedicated thermal treatment of SLM products which are guided by Differential Scanning Calorimetry of melt spun samples.

[1] N. T. Aboulkhair et. al., Metall. Mater. Trans. A 46A, (2015)

[2] S. Marola et al., J. Alloys and Compounds 742, 271 (2018)

## ID-421

**Al-Si-Ni-Cr-Fe alloy prepared by selective laser melting: microstructure and mechanical properties**

*G. Cattano*<sup>1</sup>, *R. Zhang*<sup>2</sup>, *M. Lombardi*<sup>1</sup>, *P. Fino*<sup>1</sup>, *N. Birbilis*<sup>2</sup>

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Selective laser melting (SLM) is an additive manufacturing (AM) powder-bed process in which single layers of powders are spread on a building platform and locally melted by a computer-controlled laser beam. These operations are cyclically repeated to the end of the building process and lead to the fabrication of components with sophisticated shapes but also to materials with unique microstructures as consequence of the high cooling rate experienced. In processing Al-Si alloys, such a rapid solidification (RS) process allows to obtain extended solid solutions of transition metals (TM) and the precipitation of strengthening submicrometric phases, which in turns contribute in giving alloys with enhanced mechanical properties and refined microstructures. These beneficial metallurgical effects add together to the flexibility offered by SLM in exploring new alloys and microstructures by mixing *in-situ* different powders, as reveal successful studies of the past years [1]. However, the topic is still few explored. In the present study we mixed AlSi<sub>10</sub>Mg powder with 6 wt% Hastelloy X (HX) powder, a nickel-based superalloy rich in Cr, Fe and Mo. Our results show that the microstructure consists of a homogenous distribution of TM elements within the Al matrix with local solute enriched areas as a result of the short solidification times. XRD analysis revealed the precipitation of a bcc phase, indexed as the cubic Al<sub>4.01</sub>MnSi<sub>0.74</sub> phase and marked as -Al<sub>15</sub>(Fe,Cr,Ni)<sub>3</sub>Si<sub>2</sub> and the hardness of the material increased up to 90% with respect to the standard AlSi<sub>10</sub>Mg processed by SLM. Furthermore, our results show that the alloying process strongly affects the complex consolidation phenomena that take place after laser melting, giving a material less dense than the SLM-processed AlSi<sub>10</sub>Mg alloy but also locally altering the morphology of eutectic Si network.

[1] B. Vranken, L. Thijs, J-P Kruth, J. Van Humbeeck, Acta Materialia 68, 150 (2014), <https://doi.org/10.1016/j.actamat.2014.01.018>

## ID-422

**Mechanical alloying and spark plasma sintering of nanostructured CuCrFe-TiMn(Ni) high-entropy alloys**

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Traditionally alloys were processed by adding an alloying element on a single principle element. This was done through various routes: casting, powder metallurgy route, laser cladding, etc. High-entropy alloys (HEAs) containing at least five components in equiatomic or nearly equiatomic amounts have recently been suggested to consider as new materials [1,2]. It is believed that high mixing entropy could decrease the Gibb's free energy and favor the formation of HEA-based solid solutions. Due to high entropy and complex microstructure, HEAs represent a unique class of materials with attractive combination of properties such as superior strength, high wear/corrosion resistance, good thermal stability, excellent magnetic properties, etc. HEAs can be synthesized by using the methods of vacuum arc melting, rapid solidification, and mechanical alloying (MA). MA is a high-energy ball milling process that can yield stable microstructures with better homogeneity and nanocrystalline structure. Combined use of MA with spark plasma sintering (SPS) can be expected to afford the preparation of HEAs from as-milled powders. In this work, we synthesized nanostructured CuCrFeTiMn(Ni) high-entropy alloys by mechanical alloying followed by spark plasma sintering of activated powders. The elemental powders taken in equiatomic amounts were milled (in Ar atmosphere) in an Activator 2S planetary ball mill for 240 min (694/900 rpm). Starting and milled powder mixtures were characterized by XRD, electron diffraction, high-resolution SEM/EDS, and high-resolution TEM. The stability of CuCrFeTiMn(Ni) was analyzed by differential scanning calorimetry (DSC). A bcc solid solution with refined microstructure (grain size 10 nm) could be obtained after 30 min of milling. As-milled powders of CuCrFeTi(Mn)Ni exhibited good thermal stability up to 500°C. The as-milled powders were then subjected to SPS at 600–800°C. XRD results for bulk HEAs confirmed the formation of both fcc and bcc solid solutions. The electrical resistivity of bulk specimens had a value of 1.01–6 Ω m.

This work was financially supported by the Russian Science Foundation (project no. 16-13-10431: Self-sustaining thermal waves in amorphous media).

[1] B. Cantor, I.T.H. Chang, P. Knight, A.J.B. Vincent. *Mater. Sci. Eng. A* 375-377, 213 (2004)

[2] P.-K. Huang, J.-W. Yeh, T.-T. Shun, S.-K. Chen. *Adv.Eng. Mater.* 6, 74 (2004)

**ID-385****Processes involved during nanostructured material production by Pulsed Laser Ablation in Liquid**

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During last decade the method generally named Pulsed Laser Ablation in Liquid (PLAL or simply LAL) has been widely developed for producing nanostructured materials of different kinds. In this work, it is going to be presented an overview of the processes involved during PLAL as well as some features of the generated nanostructures obtained using either metal or carbon based substrates. In order to evidence the main phenomena that are involved during PLAL and the time-scales at which they occur, different techniques, such as Optical Emission Spectroscopy (OES) and shadowgraph imaging data will be shown. In this manner, different stages of the process such as the laser induced plasma, shock wave and cavitation bubble dynamics, which occur until the generated nanoparticles are released into the solution, can be followed and surveyed. Varying some properties of the liquid or of the substrate, e.g. the liquid pressure or the typology such as bulk or wire, respectively, or the laser pulse duration, the dynamics of the PLAL features change without affecting greatly, at first glance, the produced nanoparticles.

In order to characterize these, ex-situ techniques such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Raman spectroscopy and, for noble metal colloidal solutions, in-situ Surface Plasmon Resonance (SPR) spectroscopy, are used. In some circumstances, soon after-wards the production of nanoparticles, the formation of more complex nanostructures presenting properties of interest for applications such as titania microtubes, carbon nanotubes etc. can take place. It follows that the advantages and drawbacks of the method will be outlined so that perspectives for its further development can be envisaged.

**ID-149****Cooling strategies for droplet solidification of glass forming alloys**

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The synthesis of glass forming alloys is often accompanied by nano-crystallization due to kinetically related growth or cooling rate limitations. Droplet solidification strongly depends on the convective heat release, which in turn cannot be increased considerably under regular gas atomization conditions. Alternative cooling strategies are required to increase the heat transfer coefficient and thus the cooling rate.

Gas atomization was used to produce fully amorphous soft magnetic iron-based powders by different cooling strategies (hot gas atomization and quenching). The cooling rate depends primarily on the droplet size, the heat transfer coefficient, and the temperature gradient between the melt droplet and the surrounding inert gas or quenching media. Novel cooling rate correlations were developed allowing the estimation of the cooling rate without additional gas atomization experiments. These correlations showed that the cooling rate is not only a function of the droplet size, but also a function of the process parameter gas-to-melt mass flow ratio (GMR) and the initial gas temperature. However, elevated gas temperatures have only a small impact on the cooling rate and the amorphous fraction.

The use of different quenching media increases the cooling rate by a factor of 5 when compared with convective cooling and is considered as a promising cooling strategy for glass forming alloys.

## ID-244

**Improvement of plasticity of  $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$  bulk metallic glasses by addition of Zr or Ta crystalline particles**

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Bulk metallic glasses (BMGs) are considered as potential candidates in the structural engineering fields, due to their mechanical properties. BMGs exhibit high strength, high hardness, high specific strength (strength/density), superior elastic limits (2%), high scratch and wear resistance. However, they are generally brittle and do not exhibit plastic deformation at room temperature. This lack of plasticity or ductility severely limits their structural applications. In addition, for many compositions the maximum size of the samples is limited.

To bypass this problem, metallic glass matrix composites (MGMCs) can be successfully obtained by powder metallurgy. A second phase (a crystalline one) is mixed with an amorphous powder and then the mixture is densified. The presence of secondary phases can arrest the highly localized shear bands before they can develop and become cracks, and promote the formation of profuse shear bands. The present paper addresses the manufacturing of bulk metallic composites by powder metallurgy:  $\text{Cu}_{50}\text{Zr}_{45}\text{Al}_5$  amorphous powder is mixed with different volume fraction of pure Zr or Ta crystalline particles and consolidated by spark plasma sintering (SPS). The dense composites containing crystalline particles homogeneously distributed in the amorphous matrix showed a considerable amount of plastic strain (0% for the monolithic amorphous alloy to 10% for MGMC with  $V_f = 20\%$  Ta, for ex-ample). Compressive strength and elastic modulus of composites depend on chemical composition, content and shape of crystalline particles. Composites consolidated by SPS present new possibilities of applications as they offer excellent mechanical properties and satisfying large size requirements.

**Monday 2 July morning - 11:30/13:15**

Parallel Session 4  
**CRYSTALLIZATION PROCESSES I AND MECHANICAL PROPERTIES I**  
Chair: E. S. Park

**ID-52 (Invited)****Tailoring nanocrystallization to break the speed limit of phase-change memory***E. Ma**Johns Hopkins University*

This talk describes a very recent success [1] that takes advantage of metastable alloys for nanoelectronics, setting an unprecedented operation speed for memory and switch applications. Specifically, we have designed a new phase-change alloy with drastically reduced crystal nucleation stochasticity from the parent amorphous phase. The ultrafast transition between the two metastable states accomplishes sub-nanosecond switching for cache-type phase-change random-access memory (PCRAM) technology.

Operation speed is currently a key challenge in PCRAM technology, especially for achieving sub-nanosecond high-speed cache-memory (such as SRAM). The limiting factor in the commercialized PCRAM products is the writing speed (~currently several tens of nanoseconds), which originates from the stochastic crystal nucleation during the crystallization of the amorphous Ge<sub>2</sub>Sb<sub>2</sub>Te<sub>5</sub> glass. Here we demonstrate an alloying strategy that can speed up the crystallization kinetics by orders of magnitude in phase-change memory glass. The newly designed chalcogenide alloy enables a record-setting writing speed (as short as ~700 picoseconds) in a conventional PCRAM device, with no requirement for pre-programming or additional device design. This ultrafast crystallization stems from the reduced stochasticity of nucleation via geometrically matched and robust chemical bonds that stabilize crystal precursors in the amorphous state, which are found via ab initio simulations to exhibit long life-times, shortening the incubation time for crystallization. This discovery not only is a milestone that paves the way for the development of “universal memory” using PCRAM technology to boost the working efficiency of computing systems, but also highlights materials science principles in action, offering the insight to guide the alloy design from atomic (bonding configurations and sub-critical nuclei) scale

[1] F. Rao et al., Science 358 (6369), 1423 (2017).



## ID-332

*Influence of citrate and other small dicarboxylic acids on hydroxyapatite nanocrystal nucleation, growth and surface properties*

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Hydroxyapatite (HA) nanocrystals are intriguing biominerals, whose formation in the organisms is still not completely understood. The study of HA biomineralization is crucial to understand how living organisms form their specialized mineralized structures and at the same time to achieve advanced synthetic materials. Citrate (Cit) has gained high interest since it has been proved to be a strong regulator of HA crystal growth. In particular, Cit drives the growth pathway of HA via an amorphous precursor and controls the size of nanocrystals by the non-classical oriented aggregation mechanism, forming platy crystals elongated along their c-axis. It was reported that the selectivity of Cit for the (1 0 -1 0) face of HA crystals is due to the match between the distance of surface Ca<sup>2+</sup> ions along this face and the spacing of dicarboxylates groups of Cit. Therefore, in this work HA has been synthesized in presence of hydroxycitrate (CitOH) and glutaric acid (Glr) in order to understand how small variations in Cit functional groups can affect growth and shape of HA nanocrystals. Cit-HA, CitOH-HA and Glr-HA were synthesized by a thermal decomplexing batch method, and crystals collected at different maturation times were studied by TEM, DLS, XRPD and synchrotron SAXS/WAXS. Crystal nucleation and growth was also followed by synchrotron time-resolved in situ SAXS. The experiments have revealed that CitOH is a HA crystal growth inhibitor stronger than Cit, as evinced by a longer nucleation time and a lower crystallinity degree, with smaller crystalline domains. At the same time, in comparison to Cit, it increases the surface charge and reduces the aspect ratio of the nanocrystals. On the other hand, Glr shows an opposite behavior, increasing the aspect ratio and decreasing the surface charge. It has been evinced therefore that slight variations in the citrate functional groups can significantly affect the nucleation and growth of HA nanocrystals. These results increase our knowledge on crystallization pathways of HA nanocrystals allowing the design of advanced nanoparticles with high biological performances for several nanotechnological applications. Moreover, for the first time the crystallization of HA in presence of small organic molecules has been followed in real time by in situ SAXS with synchrotron light.

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## ID-330

**Controlling the Curie temperature in amorphous glass coated microwires by heat treatment**

*A. Dzhumazoda, L. Panina, M. Nematov, A. Adam, A. Ukhasov, A. Morchenko, F. Tabarov, N. Yudanov*

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In amorphous ferromagnetic alloys of Fe-Ni compositions the Curie temperature ( $T_c$ ) can be changed by modifying the short range ordering between Ni and Fe atoms, and the kinetics of this change depends on the details of structural relaxation. In the present work, isothermal annealing was used to control  $T_c$  in amorphous  $\text{Co}_{23.67}\text{Fe}_{7.14}\text{Ni}_{43.08}\text{B}_{13.85}\text{Si}_{12.26}$  microwires. These wires have a relatively low  $T_c = 61.5$  °C and fine tuning of the critical temperature can be used in a variety of sensing applications in the important industrial temperature range. We demonstrated the abrupt change in high frequency impedance and harmonic spectra near the Curie temperature in these wires.

The annealing temperature varied from 200 °C to 500 °C, the annealing time was in the interval from 5 to 90 minutes. The Curie temperature was determined from the temperature behavior of the ac magnetic susceptibility measured by RLC meter. Depending on the annealing conditions, both the reversible and irreversible variations in  $T_c$  were achieved. For all temperatures well below the crystallization temperature (515 °C)  $T_c$  has a minimum for short annealing times. This behavior is unusual and may be related with topological short range order in alloy. The maximum decrease in  $T_c$  was observed at annealing time of 10 minutes and temperature of 350 °C. The maximum increase of  $T_c$  was observed at the annealing temperature of 500 °C which is close to the crystallization temperature. Heating below 200 °C does not affect the Curie temperature.

Thus, the Curie temperature of the investigated wires can be controlled by thermal annealing changing from 53.5 °C to 67.5 °C. Consequently, arrays of wires annealed at different conditions can be used as a sensing element operating in this temperature range.

**ID-55 (Invited)****Nanoindentation creep response of FeCoNiCrMnAl high entropy alloys over 300 to 600°C***J. Huang**City University of Hong Kong*

The creep responses under nanoindentation for the face-centered cubic (FCC) single-phased  $\text{Fe}_{20}\text{Co}_{20}\text{Ni}_{20}\text{Cr}_{20}\text{Mn}_{20}$  and the face-centered plus body-centered cubic (FCC+BCC) dual-phased  $\text{Fe}_{18}\text{Co}_{18}\text{Ni}_{20}\text{Cr}_{18}\text{Mn}_{18}\text{Al}_8$  high entropy alloys (HEAs) are examined on the FCC (111) grains over the temperature regime from 300 to 600°C, under a normalized stress level of  $2.5 \times 10^{-3}$ . The stress exponents for both alloys are both found to be about 4, or the strain rate sensitivity is about 0.25, indicating the similar dislocation climb power law creep as the controlling dominant creep mechanism. The extracted activation energy for these two under the “constant normalized stress” is  $224 \pm 12$  and  $234 \pm 10$  kJ/mol, respectively, with an average of  $\sim 230$  kJ/mol. But since there is precipitation effect in both alloys over  $\sim 400$ -600°C, the actual activation energy under the “constant structure condition” should be greater than these values, presumably about 250-280 kJ/mol. The current two HEAs possess relatively large activation energy, for example, about 150 Å at 500°C, larger than those for pure Ni or typical Ni based superalloys ( $\sim 100$  Å or less). The current creep response is compared and discussed with the Ni based superalloys.

**ID-119****Creep testing of woven fabric flax-polypropylene composite using digital correlation image (DIC)**

*R.Z. Messadi, H. Nouri, T. Hassine, M-F Lacrampe, H.B. Daly*

This paper deals with woven fabric flax-polypropylene composites materials. Specimens with a 40% fiber volume fraction were obtained by thermo-compression forming. The main objective of the current study is to investigate creep-recovery response of woven fabric flax/PP composites using the digital image correlation (DIC) technique for the entire duration of the experimenting session; the used material is characterized by a non-homogeneous structure, therefore, the use of the classical technique is not sufficient. the creep-recovery tests were performed at conditioned room (50% RH and 23°C) on the obtained specimen in wrap, weft and shear plane direction. Afterwards, the obtained data were analyzed using Findley's viscoelastic and Burgers four-element models.

Monday 2 July afternoon - 15:45/17:00

Parallel Session 1  
**METALLIC GLASSES II**  
J. Bhatt

**ID-470 (Invited)****Microporous metals by De-alloying of glasses**

*T. Spassov, L. Mihaylov, A. Inoue*

*Faculty of Chemistry and Pharmacy University of Sofia "St. Kl. Ohridski"*

It has already been established that metallic glasses can serve as suitable precursors for the formation of micro-, mezo- and nanoporous metal structures by de-alloying. These structures received an increasing research interest in the last years due to their high surface area, good electro- and thermal- conductivity, and outstanding mechanical stability associated with a wide range of applications in catalysis, sensing devices, filtering, biotechnology, etc. Most published results are on metallic glasses with appropriate content (25-35 at.%) of noble metals (Au, Ag, Pt, Pd). Though even for these glasses the mechanism of forming three-dimensional porous structure is not fully elucidated, the investigation of the process of de-alloying in non-precious metal glasses is a bigger challenge. Fewer are the publications on the latest materials as well.

The present work includes our recent results on the selective dissolution of bulk glass forming Zr- based alloys to form three-dimensional porous structures. Porous structures formed by chemical and electrochemically selective dissolution are compared. The influence of the glass composition as well as of the conditions of de-alloying on the final porous microstructure is also studied. Moreover, the evolution of the morphology and microstructure of the nanoporous material at different stages of de-alloying was investigated by electron microscopy (SEM and High Resolution TEM) and EDS microanalysis. The resulting ligaments microstructure ranges from tens to hundred nanometers. The changes in the ligament composition and microstructure at different dealloying times are correlated to the mechanism of de-alloying. Additionally, the microstructure evolution is related to the electrocatalytic activity of porous alloy. The electrocatalytic activity for Hydrogen evolution reaction of the dealloyed ribbons was found to be improved compared to the as-cast alloys.

**ID-201****Glass formation adjacent to the intermetallic compounds in Cu- Zr binary system**

*Y. Wang, J. Yao, Y. Li*

*Institute of Metal research, Chinese Academy of Science*

Traditionally, the best glass formers (e.g. alloy with the highest critical thickness) obtained through liquid quenching is usually located at or near eutectics, where the alloys are easily to bypass nucleation and/or growth of crystalline phase. Here we show that it is possible to form bulk metallic glasses near intermetallic compounds but far away from eutectics. Using Cu-Zr as a model system, we found a consistent phenomenon that two peaks in critical thickness of glass formation were located very near to  $\text{Cu}_{51}\text{Zr}_{14}$ ,  $\text{Cu}_{10}\text{Zr}_7$ , CuZr and  $\text{CuZr}_2$  intermetallic compounds, respectively. Our explanation is based on the fact that at compositions close to the intermetallic compound, the liquid phase has a lower Gibbs free energy than that of intermetallic phase. Furthermore, through the study of the viscosity of these alloys, it is evident that the crystallization of liquid of alloys close to the intermetallics is more sluggish, which provides a direct kinetic explanation. This discovery may lead to a new perspective to locate new metallic glasses.

**ID-284****A novel micro-casting process for mass production of metallic glasses microparts**

S. Gravier<sup>1</sup>, A. Lenain<sup>1</sup>, X. Cerutti<sup>1</sup>, J-J Blandin<sup>2</sup>, G. Kapelski<sup>2</sup>, R Daudin<sup>2</sup>

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Amorphous metallic alloys have attracted considerable interest during the past years due to their unique properties. One of the most impressive feature of these alloys is their capacity to couple both high structural and functional properties along with their ability to be molded like polymers. Yet, only very few industrial solutions exist and are mainly based on the manufacture of either bulk metallic glasses (such as Zr-based BMGs) or very thermally stable metallic glasses (precious metal- based). However, as almost no shrinkage occurs during their solidification upon ultra-fast cooling, they can be processed to form net shaped parts directly from the liquid state avoiding subsequent time consuming and cost-effective machining. This processing route also represent a way to process metallic glasses with poor thermal stability above  $T_g$  and low critical diameter. These aspects are very attractive for the micromechanics industries where micro parts with extreme properties are needed. The difficulty however lies in the control of the casting parameters, which can differ from one composition to another, particularly at small scales.

Recently, we have developed a highly reproducible micro-casting process specifically designed to manufacture micro parts (typically from 0.1 to several millimeters) of metallic glasses, enabling the use of a wide range of compositions. As the liquid needs to be cooled rapidly to form the amorphous structure, it becomes challenging to control the mould filling as the scale goes down. To overcome this issue, we have developed a numerical simulation code with the aim to predict the metallic liquid flow during the moulding step. Coupled with experimental results, this code enables controlling the mould filling and the fabrication of small, complex and net shaped parts.



## ID-400

**Quasicrystal-induced nucleation in a bulk glass forming Mg–Zn– Yb liquid**

*G. Kurtuldu, K.F. Shamlaye, J.F. Löffler*

We present a model alloy  $\text{Mg}_{69}\text{Zn}_{27}\text{Yb}_4$  which concurrently forms bulk metallic glass (BMG), metastable icosahedral quasicrystals (iQCs), and two crystalline approximant phases from the melt [1]. We discovered that an equilibrium approximant phase never forms directly from the melt; instead, a metastable QC phase first nucleates in the liquid and then transforms into a stable approximant phase. This path minimizes the free energy barrier for nucleation through an intermediate metastable QC phase because of the low solid–liquid interfacial energy of QCs. These observations were elaborated via a new experimental strategy of interrupted cooling after the onset of crystallization followed by an up-quenching (heating at ultrafast rates) of the previously solidified microstructure using fast differential scanning calorimetry (FDSC). Deploying this strategy, we report for the first time on the complete melting of a metastable eutectic phase mixture, including a QC phase, by suppressing the metastable-to-stable phase transition.

[1] Kurtuldu G, Shamlaye KF, Löffler JF, PNAS, accepted (2018)

**ID-234****Impact of alloying on properties and oxidation resistance of magnetron sputtered Zr–Hf–Cu based metallic glasses**

*M. Zitek, P. Zeman, M. Kotrlova, R. Cerstvy*

*University of West Bohemia*

Thin-film metallic glasses are a class of metallic alloys with an amorphous disordered structure and a viscous flow in the super-cooled liquid region. Their extraordinary properties make them promising for widespread applications, e.g. micro-electromechanical systems, diffusion barriers, surface modification of crystalline materials. One of the prerequisite to use them at elevated temperatures in air is their sufficient oxidation resistance.

Recently, we have showed that a gradual substitution of Hf for Zr in ternary Zr–Hf–Cu thin-film metallic glasses prepared by magnetron co-sputtering allowed us to tune their mechanical properties and glass transition temperature. In the present study, we focus on alloying of the Zr–Hf–Cu thin-film glasses with additional elements (X=Al, Ho, Si) up to ~15 at.% and investigation of a possibility to further tune or enhance their mechanical and thermal properties, and oxidation resistance. The films were deposited using four unbalanced magnetrons equipped with Zr, Hf, X and Cu targets in pure Ar. The magnetrons with the Zr, Hf and X targets were operated in a dc regime while the magnetron with the Cu target in a high-power impulse regime. The Zr, Hf, X and Cu contents in the films were controlled by adjusting the dc powers and the average target power in a period, respectively. The films were deposited without substrate bias voltage and external heating onto rotating substrates.

All Zr–Hf–X–Cu films investigated (up to ~15 at.% X) exhibit an X-ray amorphous structure. The glass transition detected by differential scanning calorimetry can be, however, recognized only to about 10 at.% X. An alloying with Al or Si enhances the mechanical properties of the films and the thermal stability of their amorphous state while an alloying with Ho is detrimental in this respect. In addition, Al or Si extend the width of the super-cooled liquid region of the alloys and maintain their high oxidation resistance even in the super-cooled liquid region.

Monday 2 July afternoon - 15:30/17:00

Parallel Session 2  
**NANOSTRUCTURED MATERIALS II**  
Chair: B.S. Murthy

## ID-125

**Evolution of nanoeutectic and phase stability in CoCrFeNiNb<sub>x</sub> (0.45 ≤ x ≤ 0.65) high entropy alloys***B. Chanda, J. Das*

With the increasing demand for structural applications high entropy alloys (HEA) are transpire as a new paradigm shift in material society. The designing of eutectic HEAs with a balance combination of strength and ductility is a very appealing direction. The novel quinary CoCrFeNiNb<sub>x</sub> (0.45 ≤ x ≤ 0.65) High entropy alloys (HEAs) with eutectic microstructure were designed and cast by arc melting. The phase composition, mechanical properties and stability of these alloys were investigated. The evolved microstructure in all the HEAs consist of eutectic lamellae with alternating α (γ-Ni)-FCC phase and β (HCP Fe<sub>2</sub>Nb)-type Laves phase. It was observed that x=0.45, 0.55 and 0.65 alloys contain eutectic microstructure along with proeutectic phase and at x=0.5 homogenous eutectic microstructure was obtained. The CoCrFeNiNb<sub>0.5</sub> HEA with the eutectic microstructure exhibited a relatively high combination of yield strength (2060 ± 5 MPa) and ductility (17.0 ± 0.5%). The deformation behaviour were thoroughly studied using scanning electron microscopy (SEM) and Transmission electron microscopic (TEM) image where, deformed sample shows the dislocation movement in the nanostructured FCC/Laves lamellar which improves the slip transfer at the inter- face. Further, analysis regarding the eutectic phase stability in terms of different thermodynamic parameters, atomic size radius, valence electron concentration and electronegativity were carried out. The stability of the phases in CoCrFeNiNb<sub>x</sub> and other eutectic HEAs reported in the literature, revealed that, atomic size differences (δ), and Allen electronegativity (Δχ<sub>A</sub>) are reliable parameters to predict the coexistence of eutectic BCC or FCC and TCP phases, which will evolve at δ > 3.0% and Δχ<sub>A</sub> > 5.5%.

- [1] Y. Lu, Y. Dong, S. Guo, L. Jiang, H. Kang, T. Wang, B. Wen, Z. Wang, J. Jie, Z. Cao, H. Ruan, Sci. Rep., 4 (2014) 1-5.
- [2] Y. Dong, L. Yiping, J Li, W Tongmin, L. Tingju, Intermetallics 52 (2014) 105-109.
- [3] B. Chanda, J. Das, Adv. Eng. Mater., 1700908 (2017)1-9.

## ID-139

**Abnormal grain growth mediated by fractal boundary migration at the nanoscale**

*C. Braun*<sup>1</sup>, *R. Zeller*<sup>2</sup>, *H. Menzel*<sup>1</sup>, *N. Boussard*<sup>1</sup>, *J. Schmauch*<sup>1</sup>, *K. Emil*<sup>2</sup>, *R. Birringer*<sup>1</sup>

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Despite the supposed rarity implicit in its name, abnormal grain growth (AGG) appears to be a rather common mode of coarsening in nanocrystalline materials, regardless of composition or synthesis route. In inert gas-condensed nanocrystalline Pd<sub>90</sub>Au<sub>10</sub>, thermally induced coarsening fulfills the criteria for AGG, but with an unusual twist: here, the subpopulation of abnormally growing grains sends offshoots in many directions into the surrounding matrix. Evaluating EBSD maps of the resulting microstructure, we find a fractal-like morphology characterized by a box-counting fractal dimension of ~1.2 instead of the smooth interfaces observed in conventional samples [1]. This is a rather unexpected finding, since the well-established phenomenon of curvature-driven grain boundary migration would be expected to smooth out boundary fluctuations. Consequently, nonstandard mechanisms and driving forces must be considered to account for grain growth in nanocrystalline Pd<sub>90</sub>Au<sub>10</sub>. The combination of fractal interface morphologies and slight fluctuations in crystal orientation — observed within the fractal grains — suggests that grain rotations could be involved in the growth process.

To gain further insight into the mechanisms and driving forces underlying fractal AGG, we address the following questions: What differences exist in the grain morphology of coarsened nanocrystalline PdAu alloys versus that of conventional samples prepared by melting and solidification? Is fractality correlated with local characteristics of the microstructure? Can the fractal dimension be influenced by variations in gold concentration, heating rate, or dwell time? Experimental evidence is accompanied by phase field simulations to identify which mechanism(s) contribute to fractal boundary migration in nanocrystalline metals.

[1] Braun et al., Scientific Reports 8 (2018) 1592

## ID-236

**Phase evolution and thermal stability of mechanically alloyed Al-CoCrFeNiMn high entropy alloy**

*V. Shivam, J. Basu, Y. Shadangi, M. Singh, N. Mukhopadhyay*

*Indian Institute of Technology (BHU); Varansi*

High entropy alloys (HEAs), a new class of multicomponent alloys with alloying constituents in equiatomic or near equiatomic proportions, have emerged over the last decade with technological promise. HEAs are reported to possess excellent properties over conventional alloys.

In the present work, the alloy formation, phase evolution, thermal stability and sintering behavior of AlCoCrFeNiMn, high-entropy alloy has been studied. This alloy was prepared with equiatomic proportions of elemental powders by mechanical alloying in a high-energy planetary ball mill (Retsch) PM400 up to 40 hours. Structural and microstructural characterizations were carried out by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation, scanning electron microscopy (SEM) and transmission electron microscopy (TEM TECNAI G2 T20). The NETZSCH DSC 404F was used to understand the thermal stability of the alloy powders. In this alloy system, a body-centered cubic (BCC) phase with the lattice parameter of  $2.89 \pm 0.03 \text{ \AA}$  was observed. This has also been confirmed by TEM and HRTEM imaging. The STEM-EDS mapping of the 40 h milled powder shows no segregation of the elements and suggested that all the constituent elements are incorporated in the host lattice to increase the high entropy effect. Similar BCC phase is obtained through a different milling schedule. Dynamic DSC thermogram of this alloy powder suggests that the peak temperature and heat evolution is sensitive to heating rates. This indicates that the transformation is diffusional in nature. It has been found that this alloy is stable up to  $500 \text{ }^\circ\text{C}$  ( $773 \text{ K}$ ). Heat treatment of the 40 h milled powder sample at the higher temperature ( $> 500 \text{ }^\circ\text{C}$ ) leads to the formation of FCC phase closely related to  $\text{Ni}_3\text{Al}$  type and  $\text{Mn}_3\text{Co}_7$  type intermetallic phase. As a result of the formation of these nanocrystalline phases, high entropy alloy matrix becomes richer in the remaining elements. Similar kinds of phases were evolved after sintering of the consolidated powder.

ID-222

**Development of shape memory NiTi-based nanoparticles***J-Y Kim, S-Y Kim, S-J Kim, W-H Ryu, E-S Park**Seoul National University*

It is well known that phase transformation characteristics of shape memory alloy (SMA), such as transition of martensitic start temperature ( $M_s$ ) are different at the nanoscale compared to bulk scale. Even though shape memory behaviors at the nanoscale have been actively studied, there is a lack of proper fabrication method. Although focused ion beam (FIB) is a representative method to fabricate nanoscale SMA, this method has some limitations to investigate shape memory behavior since localized heating can be induced and the high energy can affect the material's mechanical properties by inducing amorphization.

To solve this problem, the present study proposes a pathbreaking dealloying technique in phase separating alloy system as a novel "top-down" process for synthesizing SMA nano-particles. It is well known that phase separation in the liquid occurs in several alloy systems due to a large positive enthalpy of mixing between elements like Ti-Y, Ti-Gd. In our experiments, we added Gd that has a positive heat of mixing with Ti to NiTi binary system and systematically changed compositions in order to make NiTi-rich droplet structure into NiGd-rich matrix. NiGd-rich phase has been then selectively dissolved by chemical process, and clearly spherical nano-particles have been fabricated. Additionally, we systematically explored the effect of additional elements in this system. NiTi-based SMA nanoparticles have been fabricated with NiTi-(Zr,Nb,Al,Si)-Gd quaternary phase separating system. We then investigated mechanism of nanoparticles formation by analyzing the size of particles and the shape memory behavior. This study could provide a useful theoretical basis to fabricate SMA nanoparticles by dealloying technique of phase separating system, and suggest a unique pathway to investigate size effects at nanoscale SMA.

## ID-237

**Solid solutions of Ti-Zr-S as low-dimensional semiconductors with controllable bandgap**

D. Muratov<sup>1</sup>, V. Vanyushin<sup>1</sup>, D. Kuznetsov<sup>1</sup>, A. Sinitskii<sup>2</sup>, P. Jukova<sup>1</sup>, T. Martynova<sup>1</sup>

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The recent progress in low-dimensional materials research such as graphene or transition metal chalcogenides (TMC) raised a lot of interest in the synthesis of more complex layered structures that could be then exfoliated to obtain few atom thick materials. There are some reports of chemical vapour deposited TMC's with  $MX_2$  composition where (M = Mo, W, Sn; and X is chalcogen) already showing that CVD or CVT method could be used to obtain single or few-layered films and crystals. Another layered TMC material is  $TiS_3$ , which could be synthesized in bulk form as millimeter-long whiskers by direct reaction of metallic titanium and elemental sulfur in evacuated ampoules. These whiskers could be treated by ultrasound to obtain few-atoms thick crystals that were studied in field- emission diode structures with field-effect motilities up to  $43 \text{ cm}^2/V \text{ s}$  and a bangap about 1 eV. By changing titanium to zirconium this material could have a bandgap of around 2 eV, but no report on exfoliated  $ZrS_3$  whiskers is FET devices was published.

In this study, we propose the control over the bandgap of solid solutions of Ti-Zr-S by varying the ratio between Ti and Zr in the alloys produced by arc-melting technique, from which we synthesised Ti Zr S crystals by direct reaction with elemental sulfur in vacuum sealed ampoules. Produced materials were then exfoliated by scotch-tape method or ultrasound treatment in isopropyl or ethyl alcohol.

We report UV-Vis measurements of exfoliated suspensions of Ti Zr S crystals to evaluate the bandgap, which vary from 1 to 2 eV depending on the composition. Additional bands as well as significant band shift compared to pure  $TiS_3$  and  $ZrS_3$  were both observed on Raman spectra of the Ti-Zr-S solid solutions. We also studied the structure and chemical compositions of obtained crystals and developed the method to obtain stable suspensions for further research. Confirming the control over the bandgap value is a promising start for more thorough studies of charge transport in those materials for the novel electronic devices and sensors.



## ID-245

**Monte Arci obsidian: a fascinating nanocomposite for archaeometry and material science**

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<sup>3</sup> *CNR - ISM*

Obsidian has been one of the most important raw material during the Neolithic, due to its mechanical properties and workability. Its recovery in the archaeological sites is of fundamental importance, being a well-preserved material over time able to provide insights on the socio-economical organisation of the Neolithic communities. Being the geological sources limited in number, provenance studies on the artefacts permit to determine the exchange routes of this raw material. In the Western Mediterranean, only four geological sources were available at that time: Monte Arci (Sardinia), Palmarola, Lipari, and Pantelleria. Moreover, geochemical subsources can be identified within each main source, corresponding to temporally and/or spatially distinct eruptive events and characterised by different chemical composition and properties. The differences can be therefore exploited to discriminate obsidian sources and subsources and determine the provenance of the artefacts. In this work, low-cost, fast, not destructive portable X-Ray Fluorescence permitted to discriminate the four archaeologically-relevant geochemical subsources of Monte Arci obsidian (SA, SB1, SB2, SC) and to correctly assign the analysed artefacts.

Beyond its importance in archaeology, obsidian represents an interesting material due to the coexistence of glassy, micro- and nanocrystalline components, that on the one hand renders obsidian a very complex material to be studied but on the other hand allows the use of characterisation techniques commonly adopted for the study of artificial materials and rarely for natural ones. In this second part of the work, Monte Arci obsidian was studied by X-ray diffraction (XRD) and Rietveld refinement, <sup>57</sup>Fe Mössbauer Spectroscopy, DC magnetometry and Transmission Electron Microscopy (TEM, HR-TEM). Iron-containing phases like biotite, orthoferrosilite, and a nanostructured spinel iron oxide phase were revealed and quantified by Rietveld analysis on XRD data. <sup>57</sup>Fe Mössbauer Spectroscopy and DC magnetometry revealed a great variety of magnetic behaviours: paramagnetism, antiferromagnetism, ferrimagnetism, superparamagnetism, exchange bias phenomena. Finally, TEM and HR-TEM analyses allowed to visualise the morphological properties (size and shape) and distribution of the crystalline phases into/over the glassy matrix.<sup>1</sup>

[1] Mameli, V.; Musinu, A.; Niznansky, D.; Peddis, D.; Ennas, G.; Ardu, A.; Lugliè, C.; Cannas, C. *J. Phys. Chem. C* 2016, 120 (48), 27635–27645.

**Monday 2 July afternoon - 15:30/17:00**

Parallel Session 3  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES II**  
Chair: A. Santagata

**ID-453 (Invited)****Nanodiamond/polymer composites: from materials design to 3D manufacturing**

*E. Tamburri, M. Angjellari, M.L. Terranova*

*Dipartimento di Scienze & Tecnologie Chimiche - MinimaLab, Università di Roma "Tor Vergata"*

The nanodiamond produced by detonation (DND) is presently one of the most intriguing material for basic and applied researches, due to the versatility of the diamond phase and to the number of adjunctive attractive properties conferred by the confinement effects, the unusual values of surface energy, and the rich surface chemistry deriving from the synthesis procedures. In the field of polymer-based nanocomposites DND is definitely playing a primary role. In fact, the contribution of this nanomaterial is not limited only to the improvement of the basic functional properties of the host polymer matrix. DND has proven also to behave as a revolutionary filler able to modulate the structural organization of the polymer phase [1-3]. The multi-functional surfaces of diamond nanoparticles are found to provide complex interfaces where the polymer chains can arrange giving rise to hierarchical diamond/polymer structures with non-conventional geometries and peculiar functional properties [1-3]. In this view, the hybrid nanodiamond/polymer composites can be considered promising systems for the development of innovative inks for 3D printing [4], a disruptive technology that is presently gaining more and more attention due to the variety of proposed applications in several frontier fields. However, the use of such technology implies the need of producing materials with designated functionalities, that must be preserved during the 3D manufacturing process. Given their distinctive features, DND/polymer materials are ideal candidates to check if the 3D-printing procedures influence the properties imparted to the various nanocomposites by the synergistic coupling of components with different properties. At that aim, we have designed and built a dedicated 3D printing apparatus, and in parallel we have optimized proper protocols for the preparation of suitable polymer-based/ DND-containing formulations [4].

We present here a selection of DND/polymer nanocomposites that meet the requirements for additive processes, along with some examples of 3D printed objects that can operate as multifunctional platforms in several technological areas, from electronics to regenerative medicine.

[1] E. Tamburri et al. *Polymer* 52, 5001 (2011)

[2] E. Tamburri et al. *Polymer* 53, 4045 (2012)

[3] E. Tamburri et al. *Journal of Materials Chemistry C* 2, 3703 (2014)

[4] M. Angjellari et al. *Materials & Design* 119, 12 (2017)

**ID-24 (Invited)****Alloy development for additive manufacturing processes**

*P.K. Gokuldoss*

*Norwegian University of Science and Technology, Gjøvik, Norway*

Laser based powder bed fusion processes like the selective laser melting (SLM) is one of the additive manufacturing processes used to produce 3-D metal parts by selective melting of powders dictated by CAD data. Because of the high degree of freedom given by processing through additive manufacturing, it is possible to build parts with extremely complex geometries that would otherwise be difficult or impossible to produce using conventional manufacturing processes. However, until now, only conventional alloys like the  $\text{AlSi}_{10}\text{Mg}$ , 316L,  $\text{Ti}_6\text{Al}_4\text{V}$ , etc. that either are developed for cast or wrought processes have been used for fabrication. Some of the alloys work well for the additive manufacturing process like the  $\text{Al}_{12}\text{Si}$ ,  $\text{Al-Si}_{10}\text{Mg}$ , because they have good fluidity and are readily weldable. However, there are difficulties with other non-welding alloys like the 7XXX series, where cracks are readily developed during welding and hence cannot be readily fabricated by SLM. Hence, a road map for alloy development for SLM process is developed and will be discussed in detail for developing amorphous and nanocrystalline materials.

## ID-108

**Development of medium-low density TiAlVCrX high entropy alloy**

*Y.C. Liao<sup>1</sup>, T.H. Li<sup>1</sup>, S.M. Song<sup>1</sup>, P. H. Tsai<sup>1</sup>, J.S.C. Jang<sup>1</sup>, J.C. Huang<sup>2,3</sup>*

<sup>1</sup> *Department of Mechanical Engineering and institute of Materials Science and Engineering, National Central University*

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<sup>3</sup> *Institute for Advanced Study; Department of Materials Science & Engineering, City University of Hong Kong*

Besides the classic and newly refractory high entropy alloys, medium-low density high entropy alloys are the new emerging class for biomedical and transportation areas. Based on the calculation of the radius difference of each atom and the heat of mixing, the series of TiAlVCrX (X=Fe, Mn, Cu, Nb, Ta) high entropy alloys were designed and prepared by vacuum arc melting and re-melted four times for ensuring the composition homogeneity. Among all designed alloy compositions, the series of as-cast TiAlVCrFe and TiAlVCrMn alloys can form a single BCC structure, but the as-annealed alloys will present very brittle behavior due to the precipitation of intermetallic phases. Therefore, these TiAlVCr alloy were further modified by replacing the V element with Nb and Ta elements because of the similar radius of elements Nb and Ta with the other elements in this TiAlVCr HEA alloy, the less difference of element's radius will result in forming a more stable single-phase. Moreover, for reaching the goal of the medium-low density ( $< 5 \text{ g/cm}^3$ ), a fine-tuned  $(\text{TiAl})_{70}(\text{VCr})_{25}(\text{NbTa})_5$  high entropy alloy ingots were developed and produced by vacuum arc melting and drop casting, then ho-mogenized at  $1000^\circ\text{C}$  for 24h by following the HTDSC data. Finally, all as-cast and as-homogenized sample exhibit a single BCC structure and present more ductile behavior with hardness around Hv 550.

ID-394

**Generation of 3-D functional ceramics by biomorphic transformation of highly reactive inorganic precursors***A. Tampieri, S. Sprio, A. Ruffini**Institute of Science and Technology for Ceramics, National Research Council*

The present study describes a new chemical approach for 3-D ceramic development consisting in nucleation and growth of functional phases in the 3-D state where inorganic species react and transform, as building blocks of an interconnected solid structure, inspired by natural templates as a guide of the whole process. This novel paradigm is conceived to respond to the still open challenge of achieving large functional devices in the 3-D state, particularly relevant when the final goal is given by nanocrystalline, active ceramic phases. In fact, the structural consolidation of polycrystalline compounds demands the application of high-temperature sintering processes undermining functionally-relevant chemical and structural features, such as crystal disorder and site-specific ion doping. A clear example is given by ion-doped, nanocrystalline calcium phosphates (CaPs), which are widely recognized as drivers of bone regeneration, but impossible to achieve as large 3-D scaffolds effective for bone regeneration, as the sintering process converts them into stoichiometric, crystalline CaPs with low bioactivity.

Our novel approach makes use of natural templates exposed to gas mixtures at controlled pressure to activate heterogeneous gas-solid reactions with high kinetic control. The use of gas at supercritical state and the fine tuning of a superficial aqueous layer as reservoir of reacting ions permit to activate and regulate nucleation/growth phenomena in the whole solid and generate highly reactive 3-D calcium carbonate precursors. This approach uniquely allows to obtain multi-doped (with  $Mg^{2+}$ ,  $CO_3^{2-}$ ,  $Sr^{2+}$ ) nanocrystalline apatite, by subsequent low-temperature hydrothermal treatment, as highly bioactive 3-D porous scaffolds with multi-scale structural hierarchy inherited by the natural template. These features, impossible to retain with classical ceramic process, results into outstanding biologic performance, assessed by dynamic cell culture in bioreactor and by clinically-relevant *in vivo* tests showing extensive regeneration of load bearing bone segments. Besides, the association of nanostructure and multi-scale hierarchy is at the base of much higher strength and damage-tolerant performance under compression, if compared with classic porous apatite obtained by direct foaming and sintering. This new paradigm paves the way for the development of innovative functional materials, today unable by chemical and structural degradation inherent to conventional processing.

**Monday 2 July afternoon - 15:30/17:00**

Parallel Session 4  
**CRYSTALLIZATION PROCESSES II**  
Chair: E. Ma

**ID-416 (Invited)****Abnormal relaxation behavior via disordered clusters in glass forming liquid***C-W- Ryu<sup>1</sup>, J-W Kim<sup>1</sup>, T. Ishikawa<sup>2</sup>, G-W Lee<sup>3</sup>, K.F. Kelton<sup>4</sup>, E-S Park<sup>1</sup>*<sup>1</sup> *Seoul National University*<sup>2</sup> *Japan Aerospace Exploration Agency*<sup>3</sup> *Korea Research Institute of Standards and Science*<sup>4</sup> *Washington University*

Heterogeneities in metallic glasses (MGs) have been revealed experimentally through rich collection of interrelated structural and phenomenological details. However, the fundamental understanding of the development of topological and chemical short/medium range order, profoundly influential in determining the intriguing properties, remains ambiguous, although the understanding of the dynamic properties of liquids based on structural changes may help identify the origin of the liquid fragility that is of fundamental and practical importance to metallic glasses and liquids. Recent research has focused on searching for critical transitions, such as phase separation, breakdown of the Stokes-Einstein relation, and the onset of cooperative motion. However, there are qualitative assertions focused on phenomenological interpretation without detailed emphasis on their physical mechanism. In particular, a detailed study of the liquid state dynamics in multi-component metallic systems is still lacking. In the present study, we choose two bulk metallic glass (BMG)-forming alloys, ZCAA ( $Zr_{46}Cu_{37.64}Al_8Ag_{8.36}$ ) and ZCAAB ( $Zr_{46}Cu_{30.14}Al_8Ag_{8.36}Be_{7.5}$ ) as a model system for experimental investigations of dynamic heterogeneity, because these archetypal strong glasses are reported to exhibit a difference in the microscopic heterogeneity, inhomogeneous microstructure in ZCAA but not in ZCAAB. We carry out viscosity measurements of two Zr-based BMGs in a wide temperature range ((i) above melting temperature  $T_m$  and (ii) near glass transition temperature  $T_g$ ) and describe them in the classification scheme of the 'fragility' concept, in each temperature range. Furthermore, we investigate structural changes corresponding to the thermodynamic and dynamic anomalies via in situ synchrotron X-ray scattering experiments in a contactless environment using an electrostatic levitator (ESL). We demonstrate the evolution of heterogeneity using the concept of aggregation in a liquid state and conclude our discussions by connecting dynamic behavior changes in macro scale and structural changes in atomic level.



**ID-449****How to describe atomic arrangements of disordered structures**

*K. Nishio, T. Miyazaki*

*National Institute of Advanced Industrial Science & Technology*

When studying how atoms are arranged in liquids and glasses, the Voronoi tessellation is often used. By using this method, the arrangement of atoms is represented by a tiling of Voronoi polyhedra. Each polyhedron contains one atom. We can know how an atom is surrounded by its neighbors by knowing the shape of the polyhedron containing the atom. Moreover, by knowing how the Voronoi polyhedron is surrounded by other Voronoi polyhedra, we can know how the atom is surrounded by its first nearest neighbors, second nearest neighbors, third nearest neighbors, ... However, there existed no reliable method for describing complexes of polyhedra, in other words atomic arrangements. To overcome this problem, we have recently created the polyhedron and polychoron codes [Sci. Rep. 6, 23455, Sci. Rep. 7, 40269, and Nanoinformatics, 97–130, Springer, 2018.]. In this presentation, we will give a general outline of our methods.

ID-305

**Structural characterization of amorphous FeZr by EXAFS***P.E. Jönsson, G. Muscas, G. Sebastian, I.G. Serrano, R. Johansson, V.K. Mutta, R. Scheicher**Department of Physics and Astronomy, Uppsala University, Sweden*

The structural properties of  $\text{Fe}_{1-x}\text{Zr}_x$  with  $x=0.07, 0.10,$  and  $0.20$  are investigated by extended X-ray absorption fine structure (EXAFS) spectroscopy on the Fe K-edge. The thin film samples were prepared by magnetron sputtering and characterized using Rutherford backscattering spectrometry, X-ray reflectivity, and grazing incidence X-ray diffraction. Based on the results of first-principle simulations of the amorphous structures using the stochastic quenching method, we assume that the partial pair distribution functions (pPDF) for Fe-Fe and Fe-Zr pairs are the same for the three compositions if scaled with the peak position of the first peak in the pPDF. Fitting the EXAFS data for the three compositions confirms this assumption. Ion implantation of boron into the amorphous film does only cause minor changes to the amorphous structure. However, it slightly increases the Fe-Fe distances. The Fe-Fe magnetic exchange interactions increase, according to the Bethe-Slater curve, when the Fe-Fe distances increase. An increase in Curie temperature ( $T_c$ ) is indeed observed for boron doped FeZr films [1]. The higher  $T_c$  of the boron doped FeZr can be used to create magnetic embedded structures by ion implantation through a nanostructured mask. How the absence of structural boundaries affects the magnetic properties of such chemically modulated structures will be discussed.

We thank the Swedish research council (VR) and the Carl-Trygger foundation for financial support.

[1] A. Zamani et al., J. Appl. Phys. 117, 143903 (2015).

## ID-307

**The thermal stability and nucleation dynamics of metallic glasses via ultrafast Flash DSC***J. Perepezko, M. Gao**University of Wisconsin-Madison*

There are a number of glass forming alloys including Au-based and Zn-Based systems that are strong glass forming alloys with low glass transition temperatures,  $T_g$  and melting temperatures below 450°C. While the crystallization onset temperatures are also low, the crystallization kinetics in many of these systems have not been examined and analyzed quantitatively. In order to examine the thermal stability, for one Zn-based metallic glass,  $Zn_{40}Mg_{11}Ca_{31}Yb_{18}$  and one Au-based metallic glass,  $Au_{55}Pb_{22.5}Sb_{22.5}$ , the thermodynamic properties and nucleation dynamics have been determined based on the application of the novel Flash DSC with ultrafast heating and cooling rate that allows unprecedented access to the initial nucleation stage of crystallization. The critical cooling rate range for glass formation was measured along with the critical heating rate for preventing crystallization and the kinetic fragility. For the Zn-based metallic glass, a unique double-nose-shaped temperature-time-transformation (TTT) diagram between the glass transition temperature and the melting point was discovered by isothermal tests. This novel transformation path was verified to be induced by two different nucleation sites that can originate from the intrinsic structural heterogeneity of metallic glasses. The Au-based metallic glass exhibited a single-nose TTT curve for crystallization. To further investigate the properties of the nucleation sites, a heterogeneous nucleation model was developed to simulate the experimental TTT diagram and reveal the nucleation pathways. The heterogeneous nucleation model analysis approach allows for the determination of the nucleation site density and catalytic potency factors for the competing nucleation pathways. The crystallization microstructures represent a high density of nanocrystals that indicates a high nucleation rate that is consistent with the low interfacial energy and nucleation barrier that are derived from the model analysis. In spite of the high nucleation rate, bulk glass formation is realized and is linked to the delay time for transient nucleation. The kinetics measurements and the proposed nucleation model provide a basis for a heterogeneous nucleation model that accounts for the observed crystallization processes including multiple nucleation pathways in amorphous materials.

ID-296

**The anomalous breakdown of the Stokes-Einstein relation in Ge-Sb-Te and Ag-In-Sb-Te alloys and its connection to fast crystallization in the supercooled liquid***S. Wei<sup>1</sup>, C. Persch<sup>1</sup>, Z. Evenson<sup>1</sup>, M. Stolpe<sup>3</sup>, G. Coleman<sup>4</sup>, P. Lucas<sup>4</sup>, C.A. Agell<sup>5</sup>, M. Wuttig<sup>1</sup>*<sup>1</sup> RWTH Aachen University, I. Institute of Physics (IA)<sup>2</sup> Maier-Leibnitz Zentrum (MLZ), Technische Universität München<sup>3</sup> Heraeus Holding GmbH, Germany<sup>4</sup> University of Arizona, Dept. of Materials Sci & Engineering<sup>5</sup> Arizona State University, School of Molecular Sciences

The phase-change materials such as Ge-Sb-Te and Ag-In-Sb-Te alloys can be reversibly switched between amorphous and crystalline states on a timescale of nanosecond. The alloys possess unique features such as ultrafast phase switching, strong electrical/optical contrast, and relatively stable amorphous state, which are interesting for non-volatile computer memory devices and neuromorphic computing applications. Significant progress has been made on the understanding of their crystalline phases and bonding natures, the liquid-state behavior (especially supercooled liquid state) has been less explored and its connection to crystallization kinetics needs to be better understood. Here we characterize the structural relaxation times on the timescale of picosecond and the self-diffusion coefficients of the Ge-Sb-Te and Ag-In-Sb-Te alloys in a high fluidity state above their melting point using quasi-elastic neutron scattering on the time-of-flight (TOF) spectroscopy. We find experimental evidence of an anomalous breakdown of the Stokes-Einstein relation in this high atomic mobility state. The breakdown shows the same features of the well-known anomalous liquid water. We also show that the origin of this breakdown is unlikely the dynamic heterogeneities that have been usually discussed in the deeply undercooled viscous liquid. Rather it may be related to a liquid-liquid transition (and possibly a liquid-liquid critical point) hidden below the melting temperature in the supercooled liquid state. The liquid-liquid transition in supercooled phase-change materials is also a semiconductor-metal transition and a fragile-strong transition. The anomalous liquid behavior may explain why this class of material has ultrafast crystallization kinetics at high temperatures, as being favorable for fast data read/write speed in memory devices, while its amorphous phase retains relatively stable at room temperature for long-time data retention.

Monday 2 July afternoon - 17:30/18:30

Poster session 1  
**METALLIC GLASSES**  
Chair: J. Bhatt

ID-34

**Effects of the initial welding temperature on the microstructure and properties of laser spot-welded Zr-Al-Co-Ta bulk metallic glass***H-S Wang<sup>1</sup>, T-H Li<sup>1</sup>, H-G Chen<sup>1</sup>, J. S-C Jang<sup>2</sup>*<sup>1</sup> *Department of Materials Science and Engineering, I-Shou University*<sup>2</sup> *Institute of Material Science and Engineering & Department of Mechanical Engineering, National Central University*

(Zr<sub>53</sub>Al<sub>17</sub>Co<sub>29</sub>)Ta<sub>1</sub> bulk metallic glass (BMG), free of both Ni and Cu, is more promising as a bio-material due to its superior corrosion resistance and biocompatibility. However, this BMG alloy system suffers from poor glass-forming ability (GFA) when compared to the Zr-Cu-based (e.g. Zr-Cu-Ag-Al or Zr-Cu-Ni-Al) BMGs. Thus, such a low GFA may have adverse effects on its weldability. To enhance weldability, this study used a Nd:YAG laser (which produces a faster thermal cycle) in combination with a liquid cooling device (LCD) to spot weld (Zr<sub>53</sub>Al<sub>17</sub>Co<sub>29</sub>)Ta<sub>1</sub> BMG. Here, a LCD was employed to provide a variety of initial welding temperatures (IWT, from -5 °C to room temperature). After the welding process, the microstructure evolution (including parent material (PM), heat affected zone (HAZ), and weld fusion zone (WFZ)), GFA, and mechanical properties of the laser-welded samples were investigated.

Under room temperature welding, the results showed that HAZ crystallization seemed unavoidable, although WFZ is the amorphous structure. Two types of crystallines were observed in HAZ, including a large-sized and softer Zr/Al/Co phase and a nano-sized and harder Zr/Co phase. Its GFA index,  $\Delta T_x$ , was reduced significantly. When IWT decreased, a faster cooling rate was produced, and the grain size of Zr/Al/Co crystalline in HAZ was reduced. When IWF went down to 0 °C, the Zr/Al/Co crystalline was hardly observed, but the nano-sized Zr/Co phase still existed in HAZ, which resulted in a harder HAZ when compared to PM. However, when compared to that of the room temperature welding sample, the HAZ hardness of the lower IWT (e.g. 0 °C) welding sample dropped, due to a faster cooling rate that resulted in a reduction in the volume fraction of the nano-sized crystalline. Furthermore, the GFA index,  $\Delta T_x$ , of the lower IWT (e.g. 0 °C) welding sample is not substantially different to that of the PM. However, the characteristic temperatures, glass transition temperature,  $T_g$ , and crystallization temperature,  $T_x$ , of the lower IWT welding sample exhibited a tendency to increase.

ID-38

**Characterization of soft magnetic Fe-based bulk glassy/composite cores with high thermal stability prepared by powder metallurgy***A.H. Taghvaei<sup>1</sup>, J. Eckert<sup>2</sup>*<sup>1</sup> *Department of Materials Science and Engineering, Shiraz University of Technology, Shiraz, Iran*<sup>2</sup> *Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*

Fe-based bulk metallic glasses (BMGs)/composites are highly promising materials in industry, due to their superior properties, like high mechanical strength, good corrosion resistance and outstanding soft magnetic behavior. However, in many practical cases, such as power transformers or magnetic yokes, cm-sized Fe-based samples with very low coercivity or large magnetic permeability and saturation magnetization is required, which is very difficult to be obtained by conventional rapid solidification process, like copper-mold casting. On the other hand, powder metallurgy process enables fabrication of Fe-based glassy cores with non-restricted dimensions, through a suitable powder compaction process. In the current research, Fe-based BMG/composite powder cores were produced by hot pressing of glassy powders with and without surface insulation in the temperature range of supercooled liquid region, SLR. The glassy powders with a large SLR of 98 K were initially prepared by a cryogenic milling of melt-spun glassy ribbons. Subsequently, the influence of compaction temperature on microstructure, thermal behavior, density and magnetic properties of the obtained toroidal samples were systematically investigated. It was found that the powder cores fabricated at 630 K, for period of 300 s, followed by a post-annealing treatment exhibit the best soft magnetic properties. In addition, the results of the X-ray diffraction (XRD), differential scanning calorimetry and density measurements confirmed the glassy nature, high thermal stability and high relative density of the obtained bulk samples. Furthermore, the scanning electron microscopy (SEM) results demonstrated that the hot-consolidation process is able to prepare successfully a new Fe-based soft magnetic composite glassy core with a uniform distribution of a dense insulating layer between glassy grains, without any sign of chemical reaction at particles/insulation interface. It was indicated that the fabricated composites possess significantly higher initial permeability at low frequencies, and notably lower coercivity compared to conventional Fe-based crystalline powder cores. Furthermore, the complex permeability and power loss measurements showed that the addition of insulation enhances the frequency stability of initial permeability and relaxation frequency, and drastically suppresses the core loss of the compacts at 2 kHz.

**ID-61****Structure and nanomechanical properties of amorphous welds produced at reduced temperature**

*W. Pilarczyk*

*Silesian University of Technology*

At present the elements made of amorphous materials have small dimensions. The use of laser welding process will enable the increase of elements' diameter together with the enhancement of application abilities of new materials. To get exceptional properties of the material after welding process, its structure in the heat affected zone (HAZ), fusion zone (FZ) and parent material (PM) should be controlled. Crystallization process is the most commonly occurring phenomenon in HAZ during welding of bulk metallic glasses (BMGs) on iron base. The test results revealed that nucleation and the growth of crystalline phases occurs at the earliest in the HAZ. The essence of the solution of the crystallization problem is the use of laser welding process and the application of cooling system which enable temperature lowering.

The main aim of this work was laser welding of samples at reduced temperature and presentation of structure and nanomechanical properties of amorphous welds.

Because of the metastable character of the welded material and small dimensions of particular fusion weld zones, TITAN 80-300 HRTEM and Hysitron TI950 Triboindenter equipped with QScope 250 microscopic attachment with Q-WM190 scanning probe were used for structure and properties analysis. Lowering of temperature of the welded material was done by the use of specially designed cooling system based on Peltier modules.

Examination of the nanostructure of weld showed that laser welding of an amorphous material cooled to  $-15\text{ }^{\circ}\text{C}$  enables element joining without crystalline precipitation. Detailed research proved the presence of amorphous phase in parent material, heat affected zone and fusion zone.

**Acknowledgements**

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ID-62

**Structural and electrochemical study of resorbable  $\text{Ca}_{32}\text{Mg}_{12}\text{Zn}_{38}\text{Yb}_{18-x}\text{B}_x$  ( $x=1,2,3$ ) metallic glasses in Ringer's solution***R. Babilas, D. Szyba**Silesian University of Technology*

The successful production of Ca-Mg-Zn alloys confirmed that the materials demonstrated high glass-forming ability. These ternary alloys can be successfully fabricated by conventional copper-mold casting. Calcium-based metallic glasses due to their dissolution character can be used as resorbable implants. Moreover, they generate non-toxic degradation products in simulated body fluids. Nevertheless, the highest corrosion rate of currently prepared Ca-based alloys limited them in use as medical implants. The corrosion activity may be controlled by introduction of alloying elements like B or Yb. Therefore, the aim of the research is to study the effect of B addition on glass-forming ability and active behavior of Ca-Mg-Zn-Yb metallic glasses in Ringer's solution [1-3].

The studies were performed on  $\text{Ca}_{32}\text{Mg}_{12}\text{Zn}_{38}\text{Yb}_{18-x}\text{B}_x$  ( $x=1,2,3$ ) (at.%) bulk metallic glasses in the form of plates. The master alloys were produced by induction melting and copper mold casting [4,5]. The structure of samples in the as-cast state was checked by a high-resolution transmission electron microscopy (HR-TEM) and selected area electron diffraction (SAED). The biocorrosion activity of the alloys was studied by electrochemical polarization tests in Baxter Ringer's solution (8.6 g/dm<sup>3</sup> NaCl, 0.3 g/dm<sup>3</sup> KCl, 0.48 g/dm<sup>3</sup> CaCl<sub>2</sub> · 6H<sub>2</sub>O) at 37 °C. The HRTEM observations prove that structure of  $\text{Ca}_{32}\text{Mg}_{12}\text{Zn}_{38}\text{Yb}_{16}\text{B}_2$  sample does not contain any visible nanocrystals. The SAED pattern is a typical electron diffraction pattern of amorphous structure with diffused diffraction rings. However, small reflections come from nanocrystals can be noticed for  $\text{Ca}_{32}\text{Mg}_{12}\text{Zn}_{38}\text{Yb}_{17}\text{B}_1$  and  $\text{Ca}_{32}\text{Mg}_{12}\text{Zn}_{38}\text{Yb}_{15}\text{B}_3$  alloys. The corrosion potential is different for each samples tested in Ringer's solution and shifts towards the positive values with the increase of B addition. However, the best value was obtained for alloy with 2 at.% boron addition.

The work was supported by the Rector's Grant in the field of research and development, Silesian University of Technology, no.: 10/010/RGJ17/0142.

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ID-86

**Viscous flow and deformation behaviors on supercooled liquid region of Ti-based bulk metallic glass composites containing spherical B2 particles***H-S Hwan, M-S Chul, K-K Buem**Sejong University*

Bulk metallic glass composites containing micro-scale B2 particles are subject to investigation with regards to the influence of B2 particles and interfacial stress and strain distribution on the viscous flow behavior at a supercooled liquid state. An increased volume fraction of B2 particles leads to an increase of minimum viscosity and influences to viscous flow behavior before crystallization. In high temperature deformation, the bulk metallic glass shows homogeneous deformation feature. However, the heterogeneous deformation feature is found in thermoplastically deformed bulk metallic glass composite. The strong stain accumulation and sluggish viscous flow occur around B2 particles, which are caused by the heterogeneous stress distribution linked to stress concentration and shear stress impediment around B2 particles. The sluggish viscous flow of supercooled liquids around B2 particles during high temperature deformation induces an increase of viscosity and strongly affects the viscous flow behavior of Ti-based bulk metallic glass composites containing micro-scale spherical B2 particles.

ID-87

**Variations of electrical resistivity in Zr- and Ti-based metallic glasses with glass-to-quasicrystalline transformation***B. Liu, Z. Wang, F Ye**State Key Laboratory for Advanced Metals and Materials, University of Science and Technology Beijing*

The crystallization of metallic glass (MG) occurs with heat release, volume shrinkage, and electrical resistivity drastic changes due to the differences in properties between the glass and crystalline phases. Variations of electrical resistivity in  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$ ,  $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{10}Ag_{10}$  and  $Ti_{40}Zr_{25}Cu_{12}Ni_3Be_{20}$  metallic glasses with glass-to-quasicrystalline transformation were studied under both continuous heating and isothermal annealing. The precipitation of quasicrystalline as well as the size of particles were examined by HRTEM and in-situ synchronous radiation. The three MGs showed different electrical resistivity variation from each other because of the difference in both oxygen content and quasicrystalline particle size. With the highest oxygen content and largest particle size among the three alloys, the  $Zr_{69.5}Cu_{12}Ni_{11}Al_{7.5}$  MG exhibited an increment of electrical resistivity with the precipitation of quasicrystalline. Though the other two metallic glasses had similar oxygen content, they presented different variation in electrical resistivity. A long and continuous decrement of electrical resistivity from the glass transition until the completion of first-step crystallization without any slope change indicating the onset of the primary crystallization was observed in the  $Ti_{40}Zr_{25}Cu_{12}Ni_3Be_{20}$  MG with smaller particle size, while the  $Zr_{65}Al_{7.5}Cu_{7.5}Ni_{10}Ag_{10}$  with moderate particle size exhibited a slight drop of electrical resistivity with obvious slope changes indicating the onset of quasicrystalline precipitation. The result also indicated that electrical resistivity measurement, compared with TEM analysis, provides a more intuitive approach to determine different quasicrystalline transformation processes in metallic glasses.

ID-183

**Investigation of structure and thermal properties in composite materials from metallic glasses with small addition of polytetrafluoroethylene**

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Amorphous metallic glass attracted much attention since the late 1960's. There has been a lot of booming in this field for the past two decades. In spite of the fact that the strength of metallic glass is very high, its applications are not very wide due to the poor plasticity. Contemporary on the other hand, polymeric materials are known for their high ductility, low density and low strength. Therefore, it seems very attractive to produce lightweight materials having enhanced mechanical properties by obtaining metallic glass matrix composites filled with polymer. Such kind of materials will find wide applications in daily life, such as household as well as can be used in aircraft and automotive industries.

In the present work, we have attempted to obtain the composite material based on  $Al_{85}Ni_5Y_8Co_2$  metallic glass mixed with polytetrafluoroethylene (of about 1 mass %) in order to improve physical and mechanical properties. We choose the metallic glass material ( $Al_{85}Ni_5Y_8Co_2$ ) with super cooled liquid region temperature less than the viscous fluid state of the polymer (PTFE). Such difference in the glass transition temperature should help to obtain bulk metallic glass composite material, with small inclusions of polymer particles, that can improve its tribological behavior. During composite preparation, polymer material was not in viscous fluid state in order to avoid getting out of the particles shape.

The method includes the SPS consolidation of the mixture of the polymer and the metallic glass particles at the temperature range of super cooled liquid state of metallic glass. It is found that the composite samples ( $Al_{85}Ni_5Y_8Co_2$ /PTFE) have a relatively high thermal conductivity, but mechanical properties of the obtained composites were very poor. The not attractive mechanical properties of the obtained composites should be explained by the Al oxide on the surface of each particle. The values of activation energy of the crystallization process were calculated. The calculated values were close to the values obtained for the other metallic glass alloys, obtained in our previous works (Cu-based alloy, Mg based alloy etc.) [1,2].

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ID-187

**Chemical composition and various oxygen impurity levels influence on thermal properties and critical diameter of  $Zr_{48}Cu_{36}Al_{16-x}Ag_x$  alloys***P. Blyskun, T. Kulik**Faculty of Materials Science and Engineering, Warsaw University of Technology*

Authors in this work focused on the determination of the oxygen impurity level influence on the glass forming ability (GFA) of the  $Zr_{48}Cu_{36}Al_{16-x}Ag_x$  alloys ( $x=4-14$  with a step of 2 at. %). It is already well known that oxygen presence can strongly influence the GFA of Zr-based glass-forming alloys. Generally, the lower the oxygen level is, the better the GFA results. High purity of alloying elements is obligatory in case of Zr-based bulk metallic glasses (BMGs). However, even against best efforts, during elements preparation, arc melting and subsequent casting (injection copper mould casting - in this work) there is always a possibility for some additional oxygen to be inserted to the alloys.

Here, the oxygen level after samples entire preparation process was determined by the inert gas fusion method for a series of alloys with slightly different chemical composition. Then, their critical diameters ( $D_c$ ) were determined by the cone test as well as some GFA thermal indicators (such as  $T_{rg}$  or ) were calculated from the DTA curves. Not only the chemical composition influences  $D_c$  and thermal indicators but the unintentional oxygen content was also playing a non-negligible role at the same time. Authors tried to discuss both factors in the field of obtained results.

ID-208

**Design of a modular measurement system for combinatorial development of metallic glasses***D. Park, D. Lee<sup>1</sup>, D. You<sup>2</sup>, E. Cheong, I. Oh<sup>1</sup>, H. Jo, H. Zhang<sup>3</sup>, K. Kim*<sup>1</sup> *Sungkyunkwan University*<sup>2</sup> *Department of Mechanical Engineering, Sungkyunkwan University*<sup>3</sup> *School of Materials and Energy, University of Electronic Science and Technology of China*

Bulk metallic glasses typically consist of three or more elements and their properties depend largely on the compositions. For example, one atomic percent can change the glass forming ability of a Cu- Zr metallic glass system dramatically. Therefore, vast composition ranges of metallic glasses should be investigated to discover novel systems with enhanced properties. In order to efficiently characterize metallic glasses with vast composition ranges, high-throughput and combinatorial experimental techniques can be used. In this work, we use magnetron co-sputtering to fabricate combinatorial metallic glass thin film samples and use a custom-made high-throughput measurement system that allows rapid measurements of mechanical and electrical properties of the samples. The measurement system can be operated in three different measuring modes: membrane deflection experiment and nanoindentation for mechanical testing, and electrical resistivity test for resistance mapping. The developed system has displacement, force, and resistance resolutions of 5 nm, 60 nN, and 1 m $\Omega$ , respectively. Furthermore, vision control is integrated in the system to align the measurement probes to a specific position of the sample. This enable the measurements of ~200 specimens in 10 hours. We expect that the combinatorial and high-throughput technique can be used to rapidly map out mechanical and electrical properties of thin film materials and to discover novel bulk metallic glasses with enhanced properties

ID-214

## Correlation between intrinsic properties and deformation behavior of nanoscale metallic glasses

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Bulk metallic glasses (BMGs) have desirable mechanical properties such as high yield strength, high elastic limit, and relatively low elastic modulus. However, the structural applications of BMGs are limited by their brittleness caused by inhomogeneous deformation. Interestingly, it was reported that MGs have a plastic deformation mode transition depending on the sample size, especially, suppression of shear banding upon size reduction results in homogenous deformation under stress. Recently, studies on deformation behavior of nanoscale MGs using deformation map have been actively carried out to understand fundamental mechanism of deformation mode transition. In the present study, we first investigate correlation between factors influencing deformation map such as activation energy, activation volume and homogeneous deformation of nanoscale MGs. We then systematically explore deformation behavior of MGs depending on material's intrinsic properties such as Poisson's ratio and fragility by constructing deformation map of MG at the nanoscale. This study could provide a useful guideline for structural application of MGs by overcoming their catastrophic failure through plastic deformation mode transition in local region.

ID-254

**Monte Carlo simulation of magnetic phase diagrams of amorphous alloys based on rare-Earth metals***A. Bondarev, I. Pashueva, I. Bataronov**Voronezh State Technical University*

Amorphous alloys based on rare-earth metals are of great interest due to their unique magnetic properties. In this work we report on the Monte Carlo simulation of magnetic properties of binary amorphous alloys of rare-earth metals with non-magnetic 5d-transition metal (rhenium) which are not studied so far.

Using the Monte Carlo method in the frame of the Heisenberg model, the computer simulation of magnetic properties of Re-Tb and Re-Gd amorphous alloys was performed.

For pure amorphous Tb and Re-Tb amorphous alloys, the model Hamiltonian contained two terms responsible for nearest-neighbour exchange interaction between the Tb ions with the mean value  $J_0$  and for random single-ion anisotropy  $D$ . For pure amorphous Tb the dependence of the temperature of the spin-glass-like transition  $T_f$  on the  $D/J_0$  ratio was calculated. Thus, the magnetic phase diagram for an amorphous magnet with random anisotropy in the  $D/J_0 - T$  coordinates was constructed.

In the models of the Re-Tb amorphous alloys, the spin-glass-like phase transition was also observed. With increasing concentration of Tb atoms, the transition temperature linearly increases, which is in a good agreement with the experimental results. The spin-glass transition is observed only above the percolation threshold in this system, i.e. at  $x > 13$  at. % Tb.

For pure amorphous Gd and Re-Gd amorphous alloys, the model Hamiltonian contained two terms responsible for ferromagnetic exchange interaction  $J_1$  between the nearest-neighbour Gd ions and for antiferromagnetic exchange interaction  $J_2$  between the Gd ions in the second coordination sphere. For pure amorphous Gd the dependence of the spin-glass transition temperature  $T_f$  on the  $J_1/J_2$  ratio was calculated. Thus, the magnetic phase diagram for an amorphous magnet with competition of exchange interactions of different signs in the  $J_1/J_2 - T$  coordinates was constructed.

In the models of the Re-Gd amorphous alloys, the spin-glass phase transition was also observed. With increasing concentration of Gd atoms, the spin-glass transition temperature linearly increases, which is in a good agreement with the experimental results.



ID-256

**Morphological characterization of  $\text{Cu}_{47.75}\text{Zr}_{47.75}\text{Al}_{4.5}$  and  $\text{Cu}_{47.5}\text{Zr}_{45.5}\text{Al}_5\text{Er}$  bulk metallic glasses***O. Florencio, C. Lustosa<sup>1</sup>, K. Pereira<sup>1</sup>, P. Marques<sup>2</sup>, P. Silva Jr<sup>2</sup>, W. Filho<sup>2</sup>, A. Almeida<sup>3</sup>, R. Vilar<sup>3</sup>*<sup>1</sup> Mackenzie Presbyterian University<sup>2</sup> Federal University of São Carlos<sup>3</sup> CeFEMA, IST, Universidade de Lisboa

Metallic glasses have attracted the interest of many researches since their first fabrication, and seem to be promising to science and engineering. This kind of material presents superior properties compared to polycrystalline alloys with similar composition [1], such as high specific strength, high hardness and large elastic limit. The disordered structure and metastable state provide unusual structural properties and non-conventional deformation mechanisms. However, a physical understanding of the disordered structure and how it affects the properties of metallic glasses is still considered one of the great challenges in condensed matter physics and materials science [2]. In this work, a morphological characterization study of two kinds of bulk metallic glasses samples was done. The X-ray diffraction tests were done Cu  $K\alpha$  radiation ( $\lambda = 0.154$  nm). The analysis of the atomic structure of the  $\text{Cu}_{47.5}\text{Zr}_{45.5}\text{Al}_5\text{Er}_2$  alloy showed great structural disorder, and the  $\text{Cu}_{47.75}\text{Zr}_{47.75}\text{Al}_{4.5}$  sample presented peaks from crystalline phases, like  $\text{Zr}_4\text{Cu}_2\text{O}$  (big cubic phase) formed due to the affinity between zirconium and oxygen [3], into the amorphous matrix. The optical microscope was used to investigate the surface of samples. It was possible to observe a greater regularity in the surface of the  $\text{Cu}_{47.5}\text{Zr}_{45.5}\text{Al}_5\text{Er}_2$  sample than in the  $\text{Cu}_{47.75}\text{Zr}_{47.75}\text{Al}_{4.5}$ . The latter sample presents regions where dendrites formed. The Scanning Electronic Microscope used for structural analysis allowed identifying some inclusions in sample containing erbium and a few pores in the other sample. Analysis of the  $\text{Cu}_{47.75}\text{Zr}_{47.75}\text{Al}_{4.5}$  sample showed the presence of oxygen at the surface corresponding to the big cubic phase. To assess the elastic modulus and hardness of the samples a dynamic ultra-micro hardness tester with Berkovich indenter. The tests were performed using a load-creep-unload cycle, at maximum load of 500 mN. The  $\text{Cu}_{47.75}\text{Zr}_{47.75}\text{Al}_{4.5}$  sample presents an elastic modulus of  $57 \pm 20$  GPa and an indentation hardness of  $5.9 \pm 1.4$  GPa. The  $\text{Cu}_{47.5}\text{Zr}_{45.5}\text{Al}_5\text{Er}_2$  sample presents an elastic modulus of  $54.9 \pm 8.8$  GPa and an indentation hardness of  $5.8 \pm 1.0$  GPa. These results showed some degree of heterogeneity in some regions of the samples.

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ID-259

**Relationship between the mechanical properties and structural changes in Ni-(Ti, Zr, Nb, Ta) glass-forming system***H.S. Ahn<sup>1</sup>, H. Oh<sup>1</sup>, C. Ryu<sup>1</sup>, E. Park<sup>2</sup>*<sup>1</sup> *Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University*<sup>2</sup> *Seoul National University*

Ni-based metallic glasses (MG), which exhibit high thermal stability and high strength, are promising candidates for structural applications. However, up to now there is no precise direction on how to design the compositions to fine-tune the properties of MGs. Therefore, in the present study, we try to confirm the relationship between the mechanical properties and structural changes in Ni-(Ti, Zr, Nb, Ta) glass-forming system. First, we choose glass-forming Ni-TM binary alloys which have similar compositions regardless of the kind of TMs (TM=Ta, Nb, Ti, Zr). In particular, Ni<sub>60</sub>TM<sub>40</sub> and Ni<sub>40</sub>TM<sub>60</sub> compositions were chosen to compare discrete characteristics between TM solvent- rich and TM solvent border line in a binary system. To identify the role of multiple solvent constituents in TM solvent border line in binary systems, we change the number of TM from one to four with equiatomic percentage. Herein, we carefully investigate characteristics of atomic bond using high-energy X-ray data and mechanical responses through nanoindentation tests on different Ni-TM metallic glasses. This study will shed light on how to obtain tailored properties of metallic glasses for structural applications via alloy design.

ID-264

**Synthesis and characterization of bulk amorphous steel using industrial ferroalloys***C. Codrean, D. Buzdugan, I. Hulka, C. Opris**Politehnica University Timisoara*

Bulk amorphous steels (BASs) are a novel class of Fe-based bulk metallic glasses (BMGs) with a unique combination of mechanical, magnetic and chemical properties. Bulk amorphous steels having a thickness up to 12 mm were synthesized using high-purity materials (generally with the purity of higher than 99.5 wt. %) in a vacuum or controlled atmosphere. These special preparation conditions greatly increase the cost of these alloys and thus limit the development of new industrial applications. This work presents the research on the obtaining of bulk amorphous steels by water-cooled copper mold casting in an air atmosphere, using industrial ferroalloys as raw materials. The obtained samples were structurally characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC), while the mechanical properties were investigated by compression and hardness tests. The results of structural aspects and mechanical properties are promising.

**ID-279****Interfacial microstructural and mechanical properties of Ti / SUS dissimilar joints by brazing with Zr-Ti metallic glass filler***J-S Park, D-H Song, J-K Lee**Kongju National University*

Ti and Ti alloys has currently attracted significant interest in various fields of the marine industry, transportation equipment, and chemical plant industry. Thus, the requirement for dissimilar bonding with Ti and Ti alloys in various fields of products has also increased. In dissimilar bonding, it is important to obtain a uniformity of bonding interface and to control intermetallic compounds that are detrimental to mechanical properties.

In this study, we report the interfacial microstructural and mechanical properties of Ti/SUS dissimilar joints by brazing with Zr-Ti metallic glass filler. In order to control the intermetallic compound at interface, an intermediate layer with a solubility was inserted into the brazing joints. The microstructure of the brazed joint was investigated by scanning electron microscopy with electron probe micro-analysis. Mechanical properties of the joints were measured using tensile test and hardness test.

ID-306

**Swelling and structural changes in metallic glasses under swift Ion irradiation**

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Effects of irradiation with high energy heavy ions in amorphous alloy  $\text{Fe}_{77}\text{Ni}_2\text{Si}_{14}\text{B}_7$  were analyzed by Mössbauer spectroscopy, X-ray diffraction and SEM. The significant changes in the sample size during heavy ion irradiation are observed. This swelling was accompanied with amorphous matrix short-range reordering. Possible mechanisms of these phenomena are discussed.

ID-318

**Electronic structure and transport properties of  $(\text{TiZrNbCu})_{1-x}\text{Ni}_x$  metallic glasses***M. Kuveždić<sup>1</sup>, E. Tafra<sup>1</sup>, M. Basletić<sup>1</sup>, R. Ristić<sup>2</sup>, V.M. Trontl<sup>3</sup>, P. Pervan<sup>3</sup>, I. Figueroa<sup>4</sup>, E. Babić<sup>1</sup>*<sup>1</sup> *Department of Physics, Faculty of Science, University of Zagreb, Croatia*<sup>2</sup> *Department of Physics, University of Osijek, Croatia*<sup>3</sup> *Institut za fiziku, Zagreb, Croatia*<sup>4</sup> *Institute for Materials Research-UNAM, Ciudad Universitaria Coyoacan, Mexico*

We present the results of ongoing comprehensive study of the electronic properties of  $(\text{TiZrNbCu})_{1-x}\text{Ni}_x$  metallic glasses performed in a broad composition range  $x$  encompassing both, the high entropy (HE) range,  $x \leq 0.25$ , and conventional Ni-base alloy concentration range,  $x \geq 0.35$ . The electronic structure (ES) studied by photoemission spectroscopy and low temperature specific heat (LTSH) [1] reveal the split-band structure of the density of states (DoS) inside the valence band with the d-electron of Ti, Zr, Nb and also Ni present in DoS at the Fermi level  $N(E_F)$ , whereas LTSH and present magnetoresistivity results show that variation of  $N(E_F)$  with  $x$  changes in Ni-base regime. The variation of the superconducting transition temperatures,  $T_C \leq 1.6$  K with  $x$  closely follows that of  $N(E_F)$  as is usual in disordered transition metal alloys [2]. The electrical resistivities of all alloys are high ( $> 150 \mu\Omega \text{ cm}$ ) and accordingly decrease with increasing temperature over most of the explored temperature range, and their temperature dependence seems dominated by the weak localization effects over a broad temperature range (10 – 300 K). The preliminary study of the Hall effect shows that the Hall coefficient  $R_H > 0$  and in the HE concentration range change little with  $x$ . The results are compared with these for corresponding binary metallic glasses.

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ID-427

**Abnormal  $T_g$  variation in Zr-rich Zr-TM binary Metallic Glasses***K.J. Kim, W.H. Ryu, E.S. Park**Seoul National University*

Zr element has large atomic mismatch and negative enthalpy of mixing ( $\Delta H_{\text{mix}}$ ) with transition metals (TM) such as Cu, Co and Ni, which matches well with empirical rules for glass formation and causes deep eutectic compositions in Zr-TM (=Cu, Co, Ni) binary alloys. There are lots of reports on glass-forming ability (GFA) and other properties of various Zr-TM binary alloys and their variation depending on compositional changes. However, there is still insufficient understanding of the relationship between the compositional change and the property change, especially, in Zr-rich Zr-TM binary MGs. In the present study, we have systematically investigated the glass-forming region and characteristic temperature change according to the composition change in Zr-rich Zr-TM (=Cu, Co, Ni) binary alloys. Formation of amorphous phase and glass-forming region was investigated by X-ray diffraction (XRD). Simultaneously, we evaluated thermal properties such as glass transition temperature ( $T_g$ ), crystallization onset temperature ( $T_x$ ) and super-cooled liquid region ( $\Delta T_x$ ) via differential scanning calorimetry (DSC). As a result, we identified a unique phenomenon that  $T_g$  decreases as Zr content increases in Zr-rich Zr-TM binary glass forming alloys. And we found that this abnormal  $T_g$  change is closely related to the unique modulus change in Zr-rich Zr-TM binary alloys due to the compositional change. These results provide a milestone for the development of paradigm - shifting new glass-forming alloys, such as metallic glasses that exhibit superior glass-forming ability and low  $T_g$ , and thus can dramatically improve the thermoplastic formability.

ID-448

**Microstructure to magnetic properties relationship in amorphous and partially crystallized Fe-Co-Si-B-Mo-P alloy***M. Hasiak**Wrocław University of Science and Technology*

Fe-based metallic glasses are interesting from a basic research point of view because they do not show any topological order in the structural arrangement of the constituent atoms. These alloys exhibit interesting soft magnetic characteristics, i.e. high magnetic saturation, high magnetic permeability, and extremely low coercivity which are required for magnetic cores. These materials are suitable candidate for energy saving. It is well known that their microstructure and magnetic properties can be easily affected by additions such as atoms as Co, Mo, Mn, Nb, etc. and/or structural modifications that are introduced during or after the production process.

In this paper the relationship between microstructure and soft magnetic properties in the as-quenched  $\text{Fe}_{72}\text{Co}_6\text{Si}_4\text{B}_9\text{Mo}_1\text{P}_8$  precursor and after annealing above the primary crystallization temperature is studied. The sample was produced by rapid quenching method in a form of thin ribbon of about 0.025 mm thick. XRD and TEM microstructure investigations of the as-quenched  $\text{Fe}_{72}\text{Co}_6\text{Si}_4\text{B}_9\text{Mo}_1\text{P}_8$  alloy confirm amorphicity of the precursor. Crystallization kinetics investigated with a help of DSC/DTA show that only the primary crystallization temperature at about 768 K is well visible. After 30 min heat treatment at 828 K the presence of bcc Fe nanograins was observed. The annealing of the ribbon at 1150 K leads to creation of bcc FeCo and FeBP-type phases. Topography of ribbon in the as-quenched state and after annealing was analyzed by AFM/LFM in contact mode. Thermomagnetic characteristics were investigated as magnetization versus temperature  $M(T)$  in zero-field cooled mode in a wide range of temperatures (up to 1000 K) and external DC magnetic fields (up to 3 T) by VersaLab system. The Curie point of the amorphous  $\text{Fe}_{72}\text{Co}_6\text{Si}_4\text{B}_9\text{Mo}_1\text{P}_8$  alloy obtained from  $M(T)$  curve is about 640 K. The analysis of the hysteresis loops  $M(H)$  recorded at different temperatures shows that the coercivity depends on temperature and also annealing condition. Moreover, some additional investigations of microhardness with respect to Oliver-Pharr protocol for the amorphous and partially crystallized  $\text{Fe}_{72}\text{Co}_6\text{Si}_4\text{B}_9\text{Mo}_1\text{P}_8$  alloy were also performed. From obtained data it is seen that microstructure strongly affects soft magnetic properties in the  $\text{Fe}_{72}\text{Co}_6\text{Si}_4\text{B}_9\text{Mo}_1\text{P}_8$  alloy.



ID-473

**Effects of Nb minor addition on the microstructure and GFA of ZrCuAlNi bulk metallic glass***M. Samavatian<sup>1</sup>, R. Gholamipour<sup>2</sup>**<sup>1</sup> Department of Materials Engineering, Science and Research Branch Islamic Azad University**<sup>2</sup> Department of Advanced Materials and Renewable Energy, Iranian Research Organization for Science and Technology (IROST)*

In this paper, the influence of Nb element on microstructure and glass forming ability of a Zr-based bulk metallic glass was investigated. HE-XRD and DSC experiments were carried out to analyze the structural changes under minor addition of Nb. It was found that Nb can change local environments and bonds of the constituents and give rise to topological and chemical ordering. It was also revealed that the addition of Nb atoms to the BMG leads to the stabilization and the promotion of ordered clusters and their connectivity with high-coordinated polyhedra. Moreover, the results indicated that the large-sized Nb atoms can improve the atomic packing efficiency and glass forming ability.

ID-474

**Phase formation and structural evolution during annealing of Fe-SIBPCu amorphous alloys***D.P. Cabarcas, C.P. Velásquez, F.E. Echeverría, F.J.B. Osorio**Universidad de Antioquia*

For several decades FeSiB amorphous alloys have been widely used in various applications in electrical and electronic devices thanks to their soft magnetic behavior. Alloy elements such as Zr, Nb, W, Mo and Ta, among others, have been used to increase their glass-forming ability, however, this addition of elements increases the cost of the alloy and compromises its soft magnetic properties. A recent discovered multicomponent alloy formed by the elements Fe, Si, B and P has been shown to combine a good glass forming ability with good magnetic properties. This alloy, in addition to being easy to produce, represents a less expensive alloy than other types of iron-based alloys because it contains elements common in the steel industry. It has also been shown that the addition of copper to FeSiBP allows the development of a structure formed by small grains of the  $\alpha$ -Fe phase embedded in an amorphous matrix. This type of microstructure, very similar to that found in other types of iron-based nanocrystalline alloys, allows to substantially improve the soft magnetic properties of the material, giving it a high saturation magnetization and a low coercivity.

In the present work the addition of small amounts of copper in the alloy system  $(\text{Fe}_{0.77}\text{Si}_{0.08}\text{B}_{0.10}\text{P}_{0.05})_{100-x}\text{Cu}_x$  ( $X = 0, 0.25, 0.5, 0.75$  and  $1.0$ ) was studied. The alloys were processed in a single roller melt spinning device in the shape of ribbons. The structural analysis of the material and the effect of Cu on the formation of the amorphous phase was evaluated by X-ray diffraction (XRD), the thermal characteristics and thermal stability of the material were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The alloys were subjected to isothermal annealing in an inert atmosphere in order to evaluate the structural evolution and to develop a structure formed by nanometer sized crystals embedded in a remaining amorphous matrix; the structural evolution during this annealing process was studied by transmission electron microscopy (TEM) and XRD, the use of a vibrating sample magnetometer (VSM) revealed that the saturation magnetization of the material is strongly affected by the chemical composition and evolution of the phases associated with the structural changes during the annealing of the sample.

ID-479

## Preparation and properties of intermetallic low temperature MnBi phase

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Permanent magnets used in most electronic devices still rely on a certain content of rare-earth elements while the newest trend is a total reduction or substitution of those. A comfortable and simple solution is conveniently offered by magnetic Mn compounds. Magnetic properties of MnBi alloy are determined by the presence of ferromagnetic  $\alpha$ -MnBi phase. This metastable low temperature phase prepared by planar flow casting and followed by specific annealing process, has been studied by several techniques. The controlled heat treatment helps to scale up the magnetic properties (remanent magnetization, coercivity and Curie temperature) resulting from the structural transformation. We have investigated the dependence of magnetic phase content with respect to primary (nominal) chemical composition in master alloy, the structure evolution from as cast state to the required state after processing and the gradual decay of magnetic phase in time and temperature. The formation and evolution of magnetic crystalline phases was monitored by structure analysis using transmission electron microscopy and X-ray diffraction. Phase transformations in temperature and time were directly characterized by thermal analysis techniques (differential scanning calorimetry and thermogravimetry) as well as by the in-situ X-ray observation during annealing. Crystal structure of master alloy, ribbons in as-quenched as well as isothermally annealed states was investigated by X-ray diffraction. The magnetic properties via measuring the magnetic hysteresis loops were studied using vibrating sample magnetometer. Long-term time evolution of stability of structure and properties was studied at different lower temperatures on samples after the original aging process.

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ID-503

**Effect of substitution of La and Ce by Misch-metal on the glass-forming ability and thermal stability of a La-Ce-Al-Co metallic glass**

G.C. Rocco

*Department of Materials Engineering, São Carlos, Brazil*

Vitreous alloys based on rare earth elements, such as La and Ce, have been developed. Their glass transition temperatures ( $T_g$ ) are among the lowest regarding other systems and range from  $\sim 70$  °C up to  $\sim 240$  °C. Their supercooled liquid region width ( $\Delta T_x = T_x - T_g$ , where  $T_x$  = crystallization temperature) can assume values up to 86 °C with a critical diameter going up to 32 mm. Such parameters place these alloys' system as good candidates to explore processing within the supercooled liquid region since processing temperature boundary conditions are comparable to commercial polymers, e.g., PE, PP, PLA and ABS. The production and properties of metallic glasses are heavily dependents on the chemical composition. A slight variation can cause significant changes in such properties or even avoid the stabilization of the glassy or the amorphous phases and for this reason, only high purity elements are usually used. Also, La and Ce spontaneously and strongly react with oxygen, thus requiring specific care and time-consuming process on handling and portioning for alloy production. As there is a wide range of compositions based on La and Ce mixtures presenting a good glass-forming ability (GFA), this work aims to explore the production of rare earth-based glassy alloy with the substitution of high purity La and Ce by Misch-metal, which is a cheaper natural resource mainly composed by La, Ce and small portions of other rare earth metals. Ribbons, cylinders and wedge shaped samples of the  $(La_{50}Ce_{50})_{60}Al_{15}Co_{25}$  and  $(\text{Misch-metal})_{60}Al_{15}Co_{25}$  compositions were prepared by melt spinning and suction casting, respectively. Investigation of the substitution effect on  $T_g$ ,  $T_x$  and critical diameter was carried using differential calorimetric analysis, X-ray diffraction and scanning electron microscopy. The substitution by Misch-metal was able to stabilize the glassy phase. Although differences in  $T_g$ ,  $T_x$ , and critical diameters were observed, this work shows that it is possible to obtain rare-earth-based glassy alloys with high GFA by using Misch-metal. Depending on the process one wants to investigate, the Misch-metal containing alloy can be used as a cheapest and most accessible for obtaining alternative alloy.

**Monday 2 July afternoon - 17:30/18:30**

Poster session 1  
**CRYSTALLIZATION PROCESSES**  
Chair: L. Degli Espositi

ID-137

**The crystallization process of Fe based amorphous alloy***S. Hiroaki, S. Yuichi**Graduate School of Environmental Studies, Tohoku University*

Amorphous alloy which can be obtained by rapid quenching molten alloy, is a material with non-crystalline structure. The amorphous alloy has unique properties compared with the crystalline alloy, since there is no long-range order in its atomic structure. Because the structure of amorphous alloy is a metastable state, crystallization is caused by heating. Therefore, it is important to research the crystallization process of the amorphous alloy since the characteristics of amorphous alloy disappear by its crystallization.

Study on change of the structure of Fe based amorphous ribbon ( $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$ ) by annealing by using electric furnace has been carried out to make clear the crystallization process of the amorphous ribbon. The effects of process parameters in annealing, heating rate, keeping temperature and keeping time on the crystallization were investigated. In the present work, results on the microstructure and thermal property of annealed amorphous ribbon examined in detail by SEM and DSC have been reported.

ID-231

**Prediction of formation energies of interstitial atoms in HCP crystals***D. You<sup>1</sup>, M. Joo<sup>1</sup>, K. Kang<sup>2</sup>, D. Lee<sup>1</sup>*<sup>1</sup> *Departement of Mechanical Engineering, Sungkyunkwan University*<sup>2</sup> *Department of Mechanical Engineering, Yonsei University*

Formation energies of interstitial atoms are important criterion to determine stabilities of compounds. Although materials database based on ab-initio simulations (e.g. Materials Project) include formation energies of a huge number of crystal systems, data of formation energies of interstitial atoms in the crystals are not readily available. Therefore, it is often required to perform time-consuming computational works to determine the values of formation energies. In this work, several models are proposed in order to predict formation energies of impurity atoms of H, B, C, N, O, in the interstitial sites of hexagonal close-packed systems of Ti, Zr, and Hf. We use ab-initio simulations to calculate the formation energy of each crystal-interstitial system. Then, chemical and geometrical parameters, such as electronegativity, coordination number, and interstitial volumes were selected to use them as components in the prediction models. We show that several proposed prediction models, based on polynomial, n-th root, exponential, and logarithmic functions, leads to predictions of the formation energies with >96% of r-square value.

ID-272

**A study of undercooling behavior of W-Ta binary alloys in ultra-high temperature using electrostatic levitation equipment***L. H. Kim<sup>1</sup>, C. Ryu<sup>1</sup>, G. W. Lee<sup>2</sup>, E. Park<sup>1</sup>**<sup>1</sup> Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University**<sup>2</sup> Korea Research Institute of Standards and Science*

The nickel or cobalt based superalloys, which are used for high temperature structural materials, have the problem of rapidly deteriorating mechanical properties above 800°C. Thus, the degradation of physical properties in superalloys disrupts their usage in an ultrahigh temperature region. However, to be utilized as fusion reactor materials or to improve efficiency of jet engines, development of ultra-high temperature structural materials is essential. As alternative materials, ceramic based heat resistant materials are suggested. However, these materials exhibit extreme brittleness as they can be easily fractured when stress is applied. To solve this problem, refractory alloys, which have melting temperature over 2000°C, were reported to be used as ultrahigh temperature structural materials. However, the study of ultrahigh temperature properties is limited by melting of crucible, high temperature oxidation and absence of equipment which is able to heat up to ultrahigh temperature. In the present study, we systematically measure thermophysical properties of W-Ta alloys via electrostatic levitation technique. As a result, W-Ta alloys exhibit extremely deep undercooling over 600K. Microstructure depending on undercooling was investigated to investigate solidification behavior and possibility of property manipulation of W-Ta alloys. This study can provide a milestone to study of measuring thermophysical properties of refractory alloys under ultrahigh temperature.



ID-291

## Crystallization at room temperature from amorphous to tetragonal MgGa single phase

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In recent years there has been increased interest in magnesium and magnesium alloys as potential candidates for structural and also biomedical applications. Magnesium alloys show a good combination of strength and low weight making them of interest in many structural applications in automotive and aerospace industries lightweight vehicles and electronic devices as well as for biodegradable implants.

An interesting novel alloying element of Mg is gallium. So far, the number of studies on Mg-Ga alloys is rather limited and has focused mainly on the use of Mg-Ga systems as sacrificial anodes in seawater batteries and for hydrogen storage. For sacrificial anodes, Ga addition promotes the electrochemical activity of Mg due to a faster dissolution of Mg anode in environments containing aggressive ions. Concerning hydrogen storage the Mg<sub>5</sub>Ga<sub>2</sub> alloy has better hydrogen storage properties compare the pure Mg. In addition, Mg-Ga materials would also qualify for applications in medical implants. Binary alloys based on Mg-Ga showed the best results for mechanical and corrosion properties measured in 0.9 wt% NaCl solution. Moreover, cytotoxicity tests indicated that Ga had the lower toxicity, compared Sn and In, pointing out the promising use of Mg-Ga based materials as biodegradable implants.

Low density metallic alloy Mg<sub>50</sub>Ga<sub>50</sub> at.% was prepared by rapid solidification single roll melt-spinning process. Ga in the amorphous alloy has such a high diffusion rate that even at room temperature it is possible to observe progressive crystallization of the single tetragonal MgGa phase from the amorphous matrix. This phase changes orientation of its crystallites (its texture) due to extraordinary fast relaxation of internal stresses in thin ribbon.

Density, elastic modulus, hydrogen storage capacity, thermal properties of the tetragonal MgGa, will be presented. The crystal structure evolution up to its melt will be shown for the first time.

ID-381

**Comparative analysis of the transient nucleation behavior in the  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  and  $\text{Fe}_{40}\text{Co}_{40}\text{P}_{14}\text{B}_6$  glasses**S. Vasiliev<sup>1</sup>, A. Aronin<sup>2</sup>, V. Parfenii<sup>1</sup>, K. Svyrydova<sup>3</sup>, V. Tkatch<sup>3</sup><sup>1</sup>Donetsk Physics and Engineering Institute and Donbas National Academy of Engineering and Architecture<sup>2</sup>Institute of Solid State Physics of RAS<sup>3</sup>Donetsk Physics and Engineering Institute

This work is focused on experimental studies and analysis of kinetics of the  $\text{Fe}_{40}\text{Co}_{40}\text{P}_{14}\text{B}_6$  metallic glass eutectic crystallization under isothermal conditions in order to estimate the parameters characterizing transient behavior of nucleation in this alloy. The kinetic crystallization curves  $X(t)$  of the  $\text{Fe}_{40}\text{Co}_{40}\text{P}_{14}\text{B}_6$  glass were obtained from the electrical resistance measurements performed in the temperature range of 667–708 K. The Avrami exponent [1] estimated increases from 4.8 to 10.4 with increasing annealing temperature implying that the degree of non-stationarity of crystallization increases. For more detailed analysis, the experimental  $X(t)$  curves were fitted by the analytical equation [2] derived as a combination of the integral form of Kolmogorov's equation of mass crystallization kinetics [3] and the Kashchiev's transient nucleation model [4]. The model involves two variable parameters, namely, the characteristic transient time,  $\tau^{\text{ns}}$ , and the crystallization time  $\tau_c$  related to the rates of steady state nucleation and growth. The values of  $\tau_c$  and  $\tau^{\text{ns}}$  were found to strongly decreased with the annealing temperature from 13400 to 53 s and from 7030 to 737 s, respectively. The calculated from these data values of the  $\tau^{\text{ns}}/\tau_c$  ratio proposed in [2] as a measure of the transient behavior increase with increasing of annealing temperature from 0.51 to about 14 indicating about essential deviation of the nucleation rate from its steady-state value. Both characteristic times are well described by Arrhenius temperature dependencies with activation energies of about 64370 K for  $\tau_c(T)$  and 39610 for  $\tau^{\text{ns}}(T)$ .

Note that the changes of the transient nucleation rate behavior in the  $\text{Fe}_{40}\text{Co}_{40}\text{P}_{14}\text{B}_6$  glass are quite different from those found in the  $\text{Fe}_{40}\text{Ni}_{40}\text{P}_{14}\text{B}_6$  glass where the nucleation rate approaches its steady-state value with increasing of the annealing temperature [2]. The observed difference in the nucleation rate behavior is caused by the different ratio of the activation energies for  $\tau^{\text{ns}}$  and  $\tau_c$  in the FeNi- and Fe-Co-based glasses. The effect of the transient nucleation on the microstructures of crystallized glasses has been discussed.

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ID-433

**Experimental determination of the nuclei number in the deeply undercooled and rapidly solidified powder particles of the high-alloyed steel***P. Grgač, J. Mesárošová, M. Behúlová**Slovak University of Technology in Bratislava, Faculty of Materials Science and Technology in Trnava*

The solid phase crystallization in metallic melts has been a subject of the interest of scientific community as well as technological practice for many years. In technical practice, the solidification of metallic materials usually starts by heterogeneous nucleation. Homogeneous nucleation usually occurs in deeply undercooled melts. There are several published papers on modelling of homogenous nucleation in undercooled metallic melts. However, verification of the results of numerical simulations using experimental measurements is difficult, as the direct observing the homogeneous (or spontaneous) nucleation in opaque substances at high temperatures is in principle not feasible. More-over, no reliable quantitative approaches to the indirect investigation of the spontaneous nucleation in deeply undercooled metallic melts are known. This is also due to the fact that the development of final microstructure in deeply undercooled samples is influenced by thermal conditions during rapid solidification (recalescence and quasi-isothermal plateau), which usually cause morphological transformation of primary solidification formations. Consequently, experimental determination of the real number of solid phase nuclei, on which spontaneous solidification started, represents a serious problem.

The paper presents an original approach to the quantitative analysis of the crystallization nuclei number in deeply undercooled melt after spontaneous nucleation in the particles of rapidly solidified (RS) powder of Cr-Mo-V tool steel obtained by nitrogen gas atomization. In six different granulometric fractions from 50  $\mu\text{m}$  to 125  $\mu\text{m}$ , those morphological variants of primary microstructures were metallographically unambiguously identified and evaluated, in which the process of recalescence did not result in the heating of a solidifying droplet above the solidus temperature of investigated alloy, i.e. morphological characteristics of primary solidification formations were preserved. The number of nucleation events in RS particles with different diameters was found out using indirect experimental method - by counting the primary multiphase polyhedral grains on metallographic sections. The quantitative metallographic analysis applying Underwood's method revealed a non-linear dependence of the crystallization nuclei number on the particle size. The maximum volumetric density of crystallization nuclei was identified in the granulometric fraction of RS powder from 56  $\mu\text{m}$  to 63  $\mu\text{m}$ .

Monday 2 July afternoon - 17:30/18:30

Poster session 1  
**MECHANICAL PROPERTIES**  
G. Barucca

ID-23

**The microevolution of mechanical properties and microstructure in Fe-based high strength alloys with addition of immiscible elements***Y-B Jeong<sup>1</sup>, P-H Jin<sup>1</sup>, H-S Hwan<sup>1</sup>, K-J Tae<sup>2</sup>, P-S Won<sup>1</sup>, K-K Buem<sup>1</sup>**<sup>1</sup> Sejong University**<sup>2</sup> Erich Schmid Institute of Materials Science*

Eutectic alloy has high strength compared with general coarse-grained materials and it is the simple way to make ultrafine structure due to eutectic reaction. Moreover, eutectic alloy has good castability because of low melting temperature and its single reaction during solidification. However, its limited plasticity and shear localization tendency at room temperature has been considered inconsistency for commercial application. Recently, eutectic alloys have been researched that have high strength and plasticity by introducing coarse primary dendrites in eutectic matrix. In particular, reinforced mechanical properties have been obtained when the propagation of shear bands is limited in the area between the micro-scale dendrites embedded in the ultrafine eutectic matrix, preventing catastrophic failure. Therefore, it is noteworthy to develop the ductile dendrite phase reinforced ultrafine eutectic alloys by alloy designing.

In this study, we attempted to improve the mechanical properties of  $(\text{Fe}_{0.9}\text{Nb}_{0.1})_{85}\text{B}_{15}$  eutectic structure composite by adding minor elements such as Cu and Ag. Cu particles, which are immiscible with other elements, are formed in eutectic matrix and can disperse stresses during deformation. Ag also well known as an immiscible element with Fe-Nb-B composites and leads to form large volume of lamellar structure with copper during solidification by eutectic reaction. The microstructure and phase analysis were examined by using Scanning electron microscope (SEM) and X-ray diffraction (XRD). Mechanical properties were tested by Universal testing machine (UTM).

ID-56

**Fatigue response of the metastable  $Ti_{15}Mo$  and  $Ti_{12}Mo_6Zr_2Fe$  alloys treated above beta transus***L. Campanelli<sup>1</sup>, M. Santos<sup>1</sup>, A. Antunes<sup>2</sup>, P. da Silva<sup>1</sup>, C. Bolfarini<sup>1</sup>*<sup>1</sup> *Federal University of São Carlos*<sup>2</sup> *Technological Institute of Aeronautics*

Beta titanium alloys have been explored in the biomedical field due to the biocompatibility and the low modulus of elasticity. Since a satisfactory fatigue performance is required for load-bearing implants, this work aimed at the evaluation of the fatigue behavior of two metastable beta alloys,  $Ti_{15}Mo$  and  $Ti_{12}Mo_6Zr_2Fe$ , after mechanical processing and heat treatment in the beta phase field. The modulus of elasticity was around 90 GPa for both alloys. The determination of the fatigue limit with the staircase method and the Dixon-Mood statistics revealed an increased performance of the  $Ti_{12}Mo_6Zr_2Fe$  alloy, in the range of 700 MPa of maximum stress at 5 million cycles. Omega phase played a fundamental role in the fatigue response of the  $Ti_{15}Mo$  alloy.

**ID-57****Microstructure and mechanical properties of solid state welded steels***K-H Song, K-W Kim**Chosun University*

This study evaluates the microstructure development and mechanical properties of friction-welded dissimilar steels. Rod type steel materials of S20C and SC-M415H with a size of 12 mm diameter and 100 mm length were friction welded at a rotation speed of 2000 rpm and an upset force of 30 kg/cm<sup>2</sup>. Electron backscattering diffraction method was used to study the grain boundary characteristics. The mechanical properties of the welds were evaluated by Vickers microhardness and tensile tests. The application of friction welding led to grain refinement of the welds, and the average grain size at the welded zone significantly refined to 4.9 microns comparing with those of the base material zone (66.8 microns at S20C and 19.8 microns at SCM415H). The grain refinement contributed to an increase in the mechanical properties such as hardness and strength. Consequently, the Vickers microhardness and the tensile strength increased by 20 and 15%, respectively, when compared to those of the base material. Moreover, fracture occurred at the base material zone and not at the welded zone, which confirmed the soundly welded state of the steel materials.

ID-58

**Anisotropic mechanical behavior of additive manufactured AISI 316L steel***K-H Song<sup>1</sup>, Y-D Im<sup>2</sup>*<sup>1</sup> Chosun University<sup>2</sup> Yonsei University

We investigated the relationship between the microstructure and mechanical properties of additive manufactured AISI 316L steel regarding the grain aspect ratio and orientation. For this purpose, two types of specimen (vertically and horizontally built) were prepared by a selective laser melting process, and the mechanical behavior was evaluated in different tensile directions. After this, to observe the characteristic grain boundary distributions such as grain size, shape, orientation, and intergranular misorientation, electron backscattering diffraction analysis was conducted on the initial and tensile strained specimens. The specimen with a lower grain aspect ratio showed enhanced yield and tensile strengths arising from the higher strain hardening rate relative to the specimen with higher grain aspect ratio. In addition, the material composed of grains with a higher Taylor factor showed more accumulated dislocation density during tensile deformation when compared to the material composed of grains with a lower Taylor factor, which also contributed to the increase in tensile strengths because of the enhanced strain hardening rate.



ID-76

**Microstructure characterisation and mechanical properties of Al<sub>13.5</sub>Mg<sub>7</sub>Si<sub>2</sub>Cu alloy produced by rapid solidification and hot extrusion***H. Adil, S. Gerguri, F. Saporiti, J. Durodola, F. Bonatesta, F. Audebert*

The increasing pressure on automotive industry to improve engine's efficiency has led to weight reduction of key engine components such as pistons. It is known that reducing piston mass reduces dynamic or oscillating mass in an engine which decreases engine friction and therefore improves fuel consumption, power and torque. Pistons operate in high pressures and temperatures compared to other engine components and being exposed to serious mechanical and thermal conditions. The aluminium alloy widely used in pistons is Al4032 of eutectic composition (Al-12Si). In order to obtain higher strength at high temperature, a hypereutectic Al-Si alloy was developed and produced by rapid solidification. This production method allows obtaining a fine dispersion of Si particles in the aluminium solid solution matrix that cannot be obtained by conventional casting techniques for high Si content in Al alloys. The higher strength of this alloy at higher temperatures coupled with lower density makes it an ideal candidate alloy in piston applications to reduce piston mass.

The alloy Al<sub>13.5</sub>Mg<sub>7</sub>Si<sub>2</sub>Cu (w%) was provided by RSP. It was produced by rapid solidification by melt spinning followed by hot extrusion. Characterisation of the microstructure was carried out by means of optical and scanning electron microscopy with energy dispersive X-ray analysis. A microstructure formed by a fine dispersion of Si particles and intermetallics in Al solid solution matrix has been observed. The aging heat treatment conditions were investigated to determine the maximum hardness/strength (T6 condition). The hardness of the alloy increased from 97 HV in as-received state to 165 HV in T6. The hardness of the new alloy is 22% higher than the corresponding to the Al4032 (135 HV in T6). Isothermal treatments at different temperatures were carried out to investigate the thermal stability of the alloy. High temperature tensile tests results showed 2 – 4.7 times higher strength in piston operation temperature for the new alloy when compared to Al4032.

ID-104

## Influence of Mg additions, hot-extrusion, cold-rolling and artificial aging on microstructure and hardness of 2024 alloy

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The 2024 alloy exhibits excellent mechanical properties and low density. Therefore, these alloys are considered to be candidates for application in the aerospace industry. In this context, the strength improvement in 2024 alloys which is achieved by combining different processes, such as solid-solution, deformation hardening, and precipitation strengthening, is the focus of several research groups around the world as well as the present research. Respect to precipitation strengthening for this alloy, the Cu and Mg are the main alloying elements and generators of precipitates. Nonetheless, recently has been reported an increment on strength and hardness by increasing the Mg content.

The 2024 alloy and the 2024 alloy with Mg additions (0.25 wt. %) were made by conventional direct casting, the melt was degassed with argon gas (20 psi) for 5 min period and AlTiB was added as grain refiner (0.13 % wt.). Modification with Mg was performed with addition of pure Mg (99.99 %). The hot extrusion consisted of a thickness reduction in the samples (10 mm in diameter) by using indirect extrusion and an extrusion ratio of 16 at 480 °C. The solution heat treatment was done at 495 °C for 7h. Extruded samples were deformed at 5 and 15 % by cold rolling. After deformation a final aging step (195 °C) at several times was realized. The microstructural characterization was done using a SEM Hitachi model SU3500 and a TEM PHILIPS model CM-200; XRD analyses were performed in a Panalytical X'Pert PRO diffractometer. The mechanical properties were evaluated using hardness test in a LECO LM300AT microhardness tester.

The results show in both alloys, 2024 and 2024 with Mg additions, change on the microstructure of dendritic grains in as-cast condition to equiaxed grains after hot extrusion. For 2024 alloy, it is evident highest hardness value in samples after cold rolling 15%, and an increase in precipitation kinetics, which is associated to a higher number density of precipitates due major dissolution of Cu-rich phases and plastic deformation. Furthermore, it is evident the formation of Al<sub>2</sub>Cu and Al<sub>2</sub>CuMg precipitates, which are responsible of peak hardening. For 2024 alloy with Mg additions, it is evident highest hardness value in samples after cold rolling 15%, in addition, two peaks-hardening are observed, the first peak is associated to dynamic precipitation of Al<sub>2</sub>Cu and Al<sub>2</sub>CuMg phases and a second peak at 600 min aging associated to growth and loss of coherence of such phases.

ID-105

## Microstructural characterization of Al-Cu-Mg-WC composites produced by mechanical alloying and sintering process

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The metal matrix composites (MMCs) reinforced with ceramic particle is widely used in aircraft industries due to their excellent properties, like tensile strength, stability thermal and yield strength. An excellent candidate to reinforce this composite is tungsten carbide (WC) due to its high hardness, high strength, good chemical stability and better resistance at high temperature. Unfortunately, there is no literature which reports on reinforcing Al matrix using heavier refractory metal powders as reinforcements. The principal objective of this work is manufacture Al-Cu-Mg-WC composite powders by Mechanical Alloying (MA) and study their microstructural characterization and behavior in sintering process.

The experimentation consisted in fabricated by mixing powders in the appropriate percentage to obtain chemical composition of Al<sub>4</sub>Cu<sub>1.5</sub>Mg<sub>1</sub>WC (wt.%) in the alloy. It was used a high energy mill (Spex-8000) during 3 and 5 h in an argon atmosphere. The milling ball-to-powder ratio was 5 to 1, methanol was added as process control agent. The alloy powders were cold compacted at 1.8 GPa. The samples obtained were sintered at temperatures of 450, 500 and 550°C, during 3 h under argon atmosphere, the microstructural characterization was carried out by scanning electron microscopy and structural characterization was determined by X-ray diffraction. A SEM Hitachi model SU3500 and PANalytical X'Pert PRO diffractometer was used for different characterizations. The crystallite size was determined by Scherrer formula.

The particle and crystallite size, and morphology of powder changed in function of milling time because of processes of MA. In addition, it is appreciated in XRD diffractograms how decrease the intensity and broadened of characteristic peaks of Al and Cu in function of same parameter; however, the characteristic peaks of WC phase did not suffer change. On the other hand, at longer milling time, the samples sintered are more porous because of greater deformation hardening caused by MA process, whereby is more difficult consolidate the samples. In addition, from results of obtained by XRD, Vickers microhardness, density and SEM is concluded that at 3 h milling time and 450 °C of sintered temperature, the Al-Cu-Mg-WC composite shows the best mechanical behavior.

ID-145

**Mechanical properties of rapidly solidified  $\text{Ni}_3\text{Ge}$  and  $\text{Ni}_5\text{Ge}_3$  intermetallic compounds***N. Haque, R.F. Cochrane, A.M. Mullis**University of Leeds, UK*

The congruently melting, single phase, intermetallic compounds  $\beta\text{-Ni}_3\text{Ge}$  and  $\varepsilon\text{-Ni}_5\text{Ge}_3$  were produced by arc melt. Each was subject to rapid solidification via drop-tube processing. Each compound remained fully single phase  $\beta\text{-Ni}_3\text{Ge}/\varepsilon\text{-Ni}_5\text{Ge}_3$ , irrespective of the imposed cooling rate. In the investigation of  $\beta\text{-Ni}_3\text{Ge}$  compound, droplets spanning the size range  $> 850$  to  $\leq 38$   $\mu\text{m}$  diameter particles, with corresponding cooling rates of  $\leq 700$  to  $> 54500$  K/s, were subject to microstructural investigation using SEM. Six dominant solidification morphologies were identified with increasing cooling rate, namely; (i) spherulites, (ii) mixed spherulites & dendrites, (iii) dendrites - orthogonal, (iv) dendrites - non-orthogonal, (v) recrystallised, and (vi) dendritic seaweed, are observed imbedded within a featureless matrix. While, in the examination of  $\varepsilon\text{-Ni}_5\text{Ge}_3$  compound, four dominant solidification morphologies were observed, namely; (i) Partial plate & lath, (ii) plate & lath microstructure (iii) isolated hexagonal crystallites, and (iv) single crystal imbedded within a featureless matrix. Micro-Vickers hardness test result of both compounds showed that mechanical properties improve with decreasing the particle size from  $> 850$  to  $\leq 38$   $\mu\text{m}$  as a consequence of increasing the cooling rates  $> 700$  to  $> 54500$  K/s. However, on account of a microstructural transition, also observed in particular abrupt changes in micro-hardness which are coincident with changes in morphologies. These kinds of changes are observed in both compounds ( $\beta\text{-Ni}_3\text{Ge}$  and  $\varepsilon\text{-Ni}_5\text{Ge}_3$ ). Moreover, the micro-Vickers hardness results confirmed that the  $\varepsilon\text{-Ni}_5\text{Ge}_3$  (1021 Hv0.01) is significantly harder than the  $\beta\text{-Ni}_3\text{Ge}$  (526 Hv0.01) compound.

ID-157

**Effect of multi-directional forging on microstructure and mechanical properties of Al-Mg based alloy***M. Kishchik, A. Mikhaylovskaya, A. Kotov, V. Portnoy**Department of Physic Metallurgy of Non-Ferrous Metals, National University of Science and Technology "MISIS"*

Many studies focus to increasing the properties of Al-Mg based alloys by thermo-mechanical processing method that included severe plastic deformation (SPD). 1565ch alloy of Al-Mg based system (Russian grade) is used in shipbuilding, automotive and railway industries due to comparatively low cost and good mechanical and corrosion properties. Multi-directional forging (MDF) is a perspective for industrial application SPD method that accumulated large strains and produced bulk ultrafine grain materials with high mechanical and superplastic properties. This study is focused to analysis of the microstructure evolution and final properties of 1565ch alloy proceeded by MDF in a temperature range of 200 to 500°C and subsequent rolling. The applied MDF scheme accumulated the strain of 0.7 for each MDF pass and finally strain of 2.1 after one full cycle (three forging passes). The stagnant zones were observed near the surface of sample where strain is lower than in the bulk. Multistage forging eliminated the stagnant zones and increased the structure homogeneity due to dynamic recrystallization phenomena at a temperature above 350°C. Microstructure was also not uniformed at low strains in the center part of the sample. The new recrystallized grains were formed mainly near the initials high angle grain boundaries and the recrystallized fraction was increased from 60% to 85% with increasing the strain from 4.2 to 6.3. The mean recrystallized grain size was  $1.7 \pm 0.1 \mu\text{m}$  and  $1.5 \pm 0.1 \mu\text{m}$  after accumulated strain of 4.2 and 6.3 respectively. Thus the grain size insignificantly changed with the increase the amount of cycles, but homogeneity of the structure increased. MDF proceeded samples were rolled at room temperature to a sheet thickness of 1.2 mm and grain size of 3-4  $\mu\text{m}$  was achieved at recrystallization annealing. The room temperature mechanical properties and characteristics of superplasticity were analyzed. The elongation to failure up to 500% and flow stress below 20 MPa with m-value up to 0.6 were achieved at the optimum constant strain rate of  $1 \times 10^{-2} \text{ s}^{-1}$  in a temperature range of 480-540°C.

This work was financially supported by RFFI Grant N° 18-03-01115 A.

ID-178

**Interface characteristics of a Cu/Nb Clad Mg<sub>2</sub>B composite wire through deformation modes***H-G Jeong, J-B Lee, S-Y Park**Korea Institute of Industrial Technology*

Most MgB<sub>2</sub> superconducting wire was manufactured by a drawing method to obtain a desired cross-section and longitudinal-shape. In order to obtain desired cross-section and longitudinal-shape in the long and thin wire with multifilament structure, manufacturing process parameters must be precisely controlled during the creation of the wire. In the deformation process, the most important factor is to keep the interface states in harmony with material having different mechanical properties. It is difficult to reach a uniform ideal property in the coherence problems at the interface between the Cu/Nb clad metal and the Mg<sub>2</sub>B powders. Hydrostatic extrusion is very useful process for fabrication of hybrid or clad structured materials wire having different properties each other, because uniform material flow easily can be obtained during the deformation. In the present study, a cold hydrostatic extrusion process, prior to draw wire, was applied to obtain a uniform structure of Cu/Nb clad Mg<sub>2</sub>B composites at an earlier stage of a fabrication process. In order to investigate the interface characteristics depending on deformation modes, several manufacturing processes like rolling, extrusion and drawing are performed to the samples with same macro- and microstructures. As the variation of deformation modes, microstructures, interface behavior and mechanical properties were varied in the Cu/Nb clad Mg<sub>2</sub>B composites.

ID-185

## Self-reinforced composite materials based on ultra-high molecular weight polyethylene fibers

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In recent years, self-reinforced composites (SRCs) which represent composites in which a polymer matrix is reinforced with oriented fibers and tapes, or particles of the same polymer, attract particular attention of researches. The advantages of such composites are high compatibility of the matrix and the reinforcing elements, the ability to achieve a good interfacial interaction between the components of the composite and higher recyclability as compared to composites composed of different classes of components. The aim of this work is study of the structure and properties of self-reinforced composite materials based on UHMWPE fibers. For composite production compression molding method which results in only partial surface melting of UHMWPE fibers was used, during cooling the molten part formed a matrix of composite material. Self-reinforced composite materials at pressures of 0.1, 25, 50 and 75 MPa, and at temperatures 145, 155, 165 °C were obtained, the molding time for all the obtained materials was 2 minutes. It was found that the maximum values of tensile strength and Young's modulus (267 MPa and 12.6 GPa, respectively) shows the composite materials obtained at 155°C and pressure of 50 MPa. Lower temperature of compression molding (145°C) results in lower values of the tensile strength and Young's modulus (223 MPa and 8.9 GPa), and higher temperature of compression molding (165°C) results in only 43 MPa and 3 GPa, respectively. It was found that increase in compression molding temperature results in increase in fraction of the melted fibers which is accompanied by loss of unique mechanical properties of UHMWPE fibers.

Comparative studies of mechanical and tribological properties of isotropic UHMWPE and obtained composite materials were carried out. Preservation of the oriented structure of the initial fibers allows to obtain composite materials with improved properties in comparison with isotropic UHMWPE. It was found, that obtained composites shows more than 2 times lower friction coefficient and wear rate in comparison with isotropic UHMWPE. The studies showed that for isotropic UHMWPE the creep strain rate at a stress of 10 MPa was 11%, and for composites, even at a load of 150 MPa it was only 4.2%. Due to its high strength, low values of friction coefficient and wear rate, high creep resistance and biocompatibility, the developed self-reinforced composite materials can be used in various kinds of applications.

ID-197

**The microstructure and mechanical properties of Ni<sub>20</sub>Cr cold sprayed coatings***W. Żórawski<sup>1</sup>, A. Góral<sup>2</sup>, M. Makrenek<sup>1</sup>, S. Kowalski<sup>1</sup>*<sup>1</sup> *Kielce University of Technology*<sup>2</sup> *Institute of Metallurgy and Materials Science, Polish Academy of Sciences*

Cold spraying is one of the most promising and emerging technology to deposit coatings with excellent quality, low porosity, high bond strength and hardness while maintaining an original phase composition of the powder. The Ni<sub>20</sub>Cr powder (Metco 43VF-NS) was sprayed on the Al 7075 alloy by means of cold spray system Impact Innovations 5/8 with robot Fanuc M-20iA. Nitrogen was used as process gas. The microstructure and chemical composition of the powders and the coatings were analyzed by means of SEM Jeol JSM-7100 and their phase composition was studied using Bruker D8 Discover diffractometer. The micromechanical testing of coatings was carried out with the use of nanoindentation technique (Nanovea) with a Berkovitz indenter (the Olivier and Pharr methodology). The topography of the coatings after spraying was analyzed by means of a Talysurf CCI-Lite non-contact 3D profiler. The high kinetic energy of feedstock particles caused their significant deformation and particular splats strongly adhere to the substrate and to each other. Moreover, Ni<sub>20</sub>Cr cold sprayed coatings exhibit negligible porosity.



ID-207

**Development of Ion-irradiation resistant W-based alloys for fusion application***I. Oh, D. Park, K. Kim, D. Lee**Sungkyunkwan University*

Tungsten (W) has been spotlighted as a promising plasma facing material for divertors and first walls in fusion reactors due to its high melting point, good thermal conductivity, and excellent sputtering resistance. Recent studies have shown that small addition of Re or Ta in W can reduce brittleness after ion irradiation, suggesting the use of these alloys for first walls in fusion reactors. By characterizing the ion-irradiation effects on the mechanical behavior of vast composition ranges of W-based alloys, it would be possible to discover novel irradiation resistant material systems. In this work, the mechanical properties of W alloys are determined and analyzed using a high-throughput screening technique. Conventional Si-based fabrication steps and magnetron co-sputtering have been used to efficiently produce hundreds of thin film specimens with different compositions. Then the membrane deflection experiment (MDE) together with a high-throughput measurement system has been employed to determine the mechanical properties with respect to compositions of alloys. We demonstrate that this high-throughput approach can be utilized to efficiently measure the mechanical properties of a large number of W-based alloys and discover composition regimes that are irradiation damage tolerant.

ID-281

**Fatigue behavior of ultrafine-grained ferritic/martensitic steel, produced by equal-channel angular pressing***M. Nikitina, R. Islamgaliev, A. Ganeev**Institute of Physics of Advanced Materials, Ufa State Aviation Technical University*

It is known that one of the methods for increasing the fatigue endurance limit is the formation of ultrafine-grained structures that make it possible to increase the strength of most commercial metals and alloys. In ferritic/martensitic steels, the presence of dispersed particles and hard-to-deform martensite laths complicates the possibility to produce defect-free integral billets with an ultrafine-grained structure. In the present paper it is shown that in the process of equal-channel angular pressing, an ultrafine-grained structure with a mean grain size of 350 nm is formed in the ferritic/martensitic steel (C-0.14%Cr-11.53%W-1.66%Ni-1.63%Mo-45%) with the mean size of dispersed particles 60 nm, the volume fraction of which increased in the process of equal-channel angular pressing from 1.5% in the initial state to 3%. Formation of ultrafine-grained structure led to enhancement of the ultimate tensile strength to 1100 MPa and to increase of the fatigue endurance limit on the basis of 10<sup>7</sup> cycles by 20%, from 472 MPa to 570 MPa, as compared with the coarse-grained sample.

M.A. Nikitina is grateful to be supported obtaining UFG samples of steel and conducting in them TEM studies and X-ray diffraction by RFBR according to the project №18-38-00649. R.K. Islamgaliev is grateful to the Russian Ministry of Education and Science within the project part of the program for universities through project №. 16.2061.2017/4.6.

ID-292

**Effect of aluminium on superplastic behaviour and deformation mechanisms of two-phase brass***P.K. Kaboyi, O. Yakovtseva, A. Mikhaylovskaya, V. Portnoy*

NUST MISIS

Binary two-phase brass is a superplastic material highly susceptible to porosity and thus making it very inconvenient to use for superplastic forming. Large porosity develops due to grain boundary sliding (GBS), which is the predominant superplastic deformation mechanism of many alloys. Alloying with aluminium is a proven solution to this problem and could lead to improved superplastic characteristics. The objects of the investigation were alloys of the CuZn brass system of a duplex structure with addition of aluminium. Study is focused to determine the alloying effect to superplastic deformation behaviour and mechanisms.

FIB marker grids with constant line spacing were milled into the polished surface of the gauge section before deformation. Contributions of GBS were assessed based on offsets of grid lines at deformation. Significant improvement of superplastic indicators was observed due to alloying by 1%Al at 550°C. CuZn exhibits 300% elongation with GBS being main mechanism (~70% contribution) and CuZn<sub>1</sub>Al exhibits 500% elongation. Better superplasticity of CuZn<sub>1</sub>Al is the result of significant decrease in porosity after deformation due to low contribution of GBS (~30%) and intragranular deformation localised in β-phase.

Evidence of vacancy diffusion as GBS accommodation mechanisms were investigated by creating a diffusion couple using bars of brass samples as cores with tungsten wires as markers at 550°C in a carbon rich atmosphere. Analysis of Kirkendall phenomena in CuZn and CuZn<sub>1</sub>Al alloys suggested that Al alloying decreased the Cu and Zn diffusivity that is a cause of decreasing the GBS contribution and low cavitation in presence of Al.

ID-322

**Microstructural and mechanical evaluation of Nb-silicide based in-situ composite at ultrahigh-temperature***T-W Na<sup>1</sup>, J-M Park<sup>1</sup>, K-B Park<sup>1</sup>, S. Lee<sup>2</sup>, D. Kim<sup>2</sup>, K. Park<sup>1</sup>, H-K Park<sup>1</sup>, T-W Lee<sup>1</sup>*<sup>1</sup> Gangwon Regional Division, Korea Institute of Industrial Technology, Gangneung 25440, Korea<sup>2</sup> The 4th R&D institute – 4th directorate, Agency for defense development, Daejeon 34186, Korea

This study evaluated the degradation mode of Nb-silicide based in-situ composite (Nb-25Ti-16Si-8Hf-2Cr-2Al at.%) with heat treatment at 1600°C in Ar condition using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM) equipped with an energy-dispersive spectroscopy (EDS). The hardness (HRC) of specimens were decreased from about 60 to 30 with increasing time (10, 20, 30, 40, 50 hr) of heat treatment. We identified that specimens were consisted with Nbss, laves phase and two types of (Nb, Ti, Hf)<sub>5</sub>Si<sub>3</sub> that were hexagonal and tetragonal crystal structure. The results of phase transformation showed that the fraction of silicide was sharply decreased after 40 hr, and the metal substrate was increased as 41% at 50 hr. The main effect of degradation were the dissipation of silicide that caused phase separation between silicide and Ti phase due to high vapor pressure of Si. It was clearly showed the alloying design of Nb-silicide composite needs to consider that the evaporation of Si element for good oxidation resistance at high temperature.

ID-364

**Effect of Nb on microstructure and mechanical properties of Ti-based ultrafine eutectic composites***Y-S Kim, K-B Kim, P-H Jin, M-S Chul, P-S Won, S-J Kwon, S-Y Choi, Y-B Jeong, S-H Hong**Sejong University*

Ti-based nano-structured dendrite eutectic composites have been engendered considerable interest due to their good mechanical and physical properties such as high strength, high toughness, corrosion resistance and wear resistance compared to conventional microcrystalline materials. It is responsible for outstanding mechanical properties featured by the volume fraction, size, morphology, chemical composition difference and distribution of the constituent phases with different length scale, which consist of the micron-scale dendrites and the ultrafine eutectic matrix. In particular, interaction of the soft dendrite and nano-scale eutectic matrix during deformation can achieve a novel high strength composites combined with large plasticity.

In this study, the high strength  $(\text{Ti}_{82}\text{Sn}_{18})_{100-x}\text{Nb}_x$  ( $x=0\sim 15$ ) ultrafine eutectic composites with large plasticity are developed. Nb is selected because it is known as  $\beta$ -Ti stabilizer and Nb has large solubility in Ti than Sn. The addition of Nb in the Ti-Sn eutectic composite has a strong effect to decrease the size of the duplex colony and to increase the volume fraction of the  $\beta$ -Ti solid solution phase. Finally, the alloy is composed of a single  $\beta$ -Ti solid solution phase. These micro-structural evolutions in Ti-Sn-Nb alloys are effective to improve both strength and plasticity. In particular,  $(\text{Ti}_{82}\text{Sn}_{18})_{100-x}\text{Nb}_x$  alloy with  $x=11$  exhibit excellent combination of the high yield strength ( $\sim 1327$  Mpa) and large plasticity ( $\sim 36.5$  %) at room temperature compression.

**ID-373****Investigation the mechanical properties of Al–Si alloys by nanoindentation***M. Abas**Metallurgy and material science test lab (MMST), physics department, Faculty of Science, South Valley University, Qena, Egypt*

Nanoindentation tests were done on AlSi alloys. Distributions of hardness and reduced modules values were calculated on the basis of 400 indentation tests for each sample. Increase of the widths and shift of the average hardness and reduced modules to higher values were observed with increasing of the Si%, strain hardening is clear observed. Hardness maps and reduced modules were introduced.

ID-428

**Ductile martensitic steel by introducing carbon heterogeneity via ultrafast heat treatment***A.P. Mahendradhany<sup>1</sup>, K.S. Park<sup>2</sup>, Y.G. Ko<sup>1</sup>**<sup>1</sup>Yeungnam University**<sup>2</sup>POSCO Steel Company*

The present work reported the influence of carbon heterogeneity on microstructure evolution and mechanical properties of low-carbon steel. The low-carbon martensitic steel was subjected to Ultra- fast Heat Treatment (UHT) at 1173 K for 1 s with a heating rate of  $\sim 300$  K/s. For a comparison, the same sample was treated at 1173 K for 1800 s with a heating rate of  $\sim 1$  K/s to get a fully homogeneous martensitic steel. From microstructure observation, UHT sample revealed an ultrafine hierarchy of martensite with the presence of carbon-depleted zone. This was attributed to the carbon heterogeneity occurred during fast heating due to insufficient time for a complete transformation, which would alter the as-quenched microstructure. In addition, the UHT sample showed outstanding strength and ductility of  $\sim 1.5$  GPa and  $\sim 10$  %, respectively, which was  $\sim 50$  % tougher as compared to the conventional martensitic steel. The interplay between microstructure and mechanical properties would be elaborated, giving us a new insight to fabricate ductile martensitic steels.

ID-431

**Anisotropy of the mechanical properties of crystals partially stabilized zirconia**

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Crystalline materials based on partially stabilized zirconia have promising properties in many applications, both from a scientific and practical point of view. The urgency of creating such materials is determined by the prospects for their use as engineering nonmetallic high-strength and wear-resistant materials, thermal barrier and protective coatings, and also as bioinert materials for medicine. Unlike ceramic materials of similar composition crystals have an anisotropy of mechanical properties depending on the crystallographic direction, which must be taken into account in the practical application of the material.

In this study, crystals of partially stabilized zirconia with an yttrium oxide concentration of 2 to 4 mol% were grown by directional crystallization of the melt in a cold container. The method of indentation was used to measure microhardness and fracture toughness. Analysis of the anisotropy of mechanical properties was carried out on different crystallographic faces with different orientations of the diagonals of the indenter. It was found that the microhardness depends weakly on the crystallographic orientation, while the fracture toughness values for different planes differ. The maximum fracture toughness values were on a sample cut out of the crystal perpendicular to the  $\langle 100 \rangle$  direction with an orientation of the diagonals of the indenter in the  $\langle 100 \rangle$  direction. Investigations of the phase composition inside and around indentator indentations on  $\{100\}$ ,  $\{110\}$  and  $\{111\}$  planes by the method of local Raman spectroscopy were carried out. An estimate of the intensity of the tetragonal-monoclinic transition on different crystallographic planes and for different orientations of the diagonals of the indenter showed that there is an anisotropy of the tetragonal-monoclinic transition affecting the hardening transformation mechanism. The maximum amount of the monoclinic phase is found around the indentator imprint on the  $\{100\}$  plane, with the orientation of the diagonals of the indenter in the  $\langle 100 \rangle$  direction. Also, the maximum crack resistance value is realized on the  $\{100\}$  plane with the same orientation of the diagonals of the indenter. With this orientation of the diagonals of the indenter, the maximum acting stresses are obtained along the coherent planes of conjugation of the tetragonal and monoclinic phases  $(100)_t || (100)_m$  and  $[001]_t || [010]_m$ .

Acknowledgements: The work was carried out with financial support in part from the RSF (№18-13- 00397).



**PLENARY LECTURE**

Chair: D. Fiorani

**Smart magnetism: nanomaterials design for friction less transport, refrigeration and theranostics**

M. Farle

*Faculty of Physics, Universitat Duisburg-Essen, Duisburg, Germany*

Magnets are key components of energy-related technologies, such as direct drive wind turbines, e-mobility and magnetic refrigeration. They are also important in robotics and automation, sensors, actuators, and information technology. Additive manufacturing (AM) as well as controlled phase-decomposition of complex alloys are promising pathways to design magnetic materials with properties tailored to specific applications. Such novel approaches require the use of functionalized nanomagnets at length scales between few nanometers and several micrometers. Starting with a discussion of basic concepts of magnetic properties with a focus on how to tune parameters in a nanomagnet, I will highlight selected state-of-the-art experimental approaches [1,2] that allow us to experimentally analyze multifunctional particles with single particle or even atomic precision. The apparently complex behavior of hybrid metal/metal, metal/oxide, or oxide/oxide interface materials –core-shell materials - can be understood from the three fundamental interactions in magnetism: magnetic exchange due to orbital overlap, spin-orbit interaction due to inner- and intra-atomic relativistic effects (e.g., crystal field effects) and the long-range magnetic dipolar interaction. Several examples will be presented, including the formation of above-room-temperature ferromagnetic interface layers between core/shell antiferromagnetic shells, the design of a macroscopic magnet with a monopole-like magnetic response [3] and the first magnonic dispersion measured in single magnetotactic bacteria.

Work supported by European Union and Deutsche Forschungsgemeinschaft. The fruitful collaboration with many colleagues and students is thankfully acknowledged.

[1]M. Farle, Imaging techniques: Nanoparticles atoms pinpointed NATURE (News and Views) 542, 35 (2017)

[2]Z.A. Li, et al., Magnetic Skyrmion Formation at Lattice Defects and Grain Boundaries Studied by Quantitative Off-Axis Electron Holography, Nano Lett. 17, 1395 (2017) and Nat. Comm. 8, 15569 (2017)

[3]F. Scheibel, D. Spoddig, R. Meckenstock, A. Çakır, M. Farle and M. Acet, Shell-ferromagnetism in a Ni-Mn-In off-stoichiometric Heusler studied by ferromagnetic resonance, AIP Advances 7, 056425 (2016)

**Tuesday 3 July morning - 10:00/11:00**

Parallel Session 1  
**NANOSTRUCTURED MATERIALS III**  
Chair: P.S. Normile

## ID-175 (Invited)

**Tunable single-phase magnetic behavior in chemically synthesized  $\text{AFeO}_3$ - $\text{BFe}_2\text{O}_4$  (A = Bi or La, B = Co or Ni) nanocomposites**

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Magnetic nanocomposites (MN) with tailored properties are of immense scientific and technological interest. The field of MN covers a vast variety of different materials and material combinations, and a large field of applications (ranging from technical to biomedical). The properties of MN rely strongly on the interplay between those of the constituent components. One subset of MN comprises of nanocomposites consisting of strongly correlated electron oxides (SCEO) as the individual components. SCEO are complex systems, with the existence of many competing states. They are an extremely interesting class of materials even in the bulk, single phase form owing to their cross-correlated electronic and magnetic properties. The complexities only increase when the particle size is reduced to the nanoscale regime, and furthermore, two such materials are combined to form nanocomposites. In such complex systems, it becomes extremely important to be able to control the properties, without which practical applications become impossible.

Here, we demonstrate an easy, but effective method to synthesize and tune the magnetic properties of nanocomposites consisting of SCEO systems as the individual components. Our method is based on a novel synthesis technique by which the two components of the nanocomposite can be directly integrated with each other, yielding homogeneous samples with magnetic behavior reminiscent of a single phase. This technique yields superior quality samples compared to samples prepared via simple physical mixing of the two phases that have been reported to lack sufficient coupling between the two phases. We illustrate our method using multiferroic  $\text{BiFeO}_3$  and  $\text{LaFeO}_3$  as the major phase (matrix). Furthermore, we show that by a careful selection of the second magnetic phase in the nanocomposite, it is possible to customize the magnetic properties of the matrix. We illustrate this by choosing  $\text{CoFe}_2\text{O}_4$  and  $\text{NiFe}_2\text{O}_4$ , two oxides with widely differing magnetic anisotropies, as the second phase, and demonstrate a striking tuning of the magnetic coercivity of the matrix depending on the choice of the second phase in the nanocomposites. We believe that these results will be of immense value in the quest for nanocomposites with functional properties such as multiferroic nanocomposites and nanocomposites that can be used as permanent magnets.

We thank the Carl Trygger Foundation, the Wenner-Gren Foundation and the Swedish Research Council (VR) for financial support.

ID-246

**Bimagnetic spinel ferrite core-shell nanoparticles for magnetic fluid hyperthermia**

*M. Sanna Angotzi<sup>1</sup>, V. Mameli<sup>1</sup>, C. Cara<sup>1</sup>, A. Musinu<sup>1</sup>, A. Ardu<sup>1</sup>, D. Niznansky<sup>2</sup>, H. Xin<sup>3</sup>, C. Cannas<sup>1</sup>*

<sup>1</sup> University of Cagliari

<sup>2</sup> Charles University of Prague

<sup>3</sup> Brookhaven National Laboratory

In the last decade, there has been increasing interest towards the synthesis of exchange coupled bi-magnetic hard/soft and soft/hard core/shell nanoparticles, due to their various applications, such as magnetic fluid hyperthermia (MFH). Among the proposed materials, spinel ferrites ( $MFe_2O_4$ ,  $M = Fe(II), Co(II), Mn(II), etc.$ ) are the most interesting, due to the possibility to finely tune the magnetic behaviour varying size, shape, and type of the divalent cation. The chemical composition may lead to hard or soft ferrimagnetic (FiM) phases. Thanks to the structural similarities, it is possible to create core-shell architectures by an epitaxial growth of one phase on the pre-existing one, through the so-called seed-mediated growth method. Generally, this method is conducted via high temperature surfactant-assisted thermal decomposition of organometallic precursors, which allows a good control of the shell growth and high crystallinity. Nevertheless, because of the high amount of toxic organic solvents, alternative methods that preserve the advantages of the thermal decomposition but use lower temperature and low-boiling solvents are still demanded.

In this work, a low-cost seed-mediated growth strategy in solvothermal conditions was used to synthesize core-shell nanoparticles made of hard ( $CoFe_2O_4$ ) and soft ferrite spinel phases ( $\gamma-Fe_2O_3, MnFe_2O_4$ ). [1] The nanoparticles show a spinel structure (XRD), spherical shape, low dispersity (TEM and HRTEM) and are capped by a monolayer of oleate molecules (TGA and FTIR). The chemical mapping at atomic level by the combined use of STEM-EDX and STEM-EELS techniques confirmed the formation of a core-shell structure and provided details on the hard/soft interfaces. MFH measurements conducted on the water dispersion of the samples highlighted that the core-shell FiM-FiM architectures could be considered as promising systems showing increased heat release with respect to the corresponding cores. Among the diverse set of samples, those with maghemite shell showed higher SAR values. Magnetic measurements combined with  $^{57}Fe$  Mössbauer Spectroscopy were used to justify and understand the correlation between the hyperthermic behaviour and the magnetic properties, as well as the composition, the structure, and the spin disorder.

[1] Sanna Angotzi et al., ACS Nano, 2017, 11(8), pp 7889-7900.

ID-420

## The effect of Zn-substitution on magneto-structural properties of cobalt ferrite nanoparticles

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Cobalt ferrite ( $\text{CoFe}_2\text{O}_4$ ) has recently attracted considerable attention due to its potential applications in data storage, catalysis, energy, environment, and in particular, biomedicine. The partial substitution of  $\text{Co}_{2+}$  ions with less toxic zinc ions ( $\text{Zn}_{2+}$ ) has been proposed in order to tune the magnetic properties of  $\text{CoFe}_2\text{O}_4$  and to lower the potential toxicity of cobalt ions ( $\text{Co}_{2+}$ ).

In the present work, the influence of Zn-substitution on the magneto-structural properties of solvothermally derived  $\text{CoFe}_2\text{O}_4$  nanoparticles ( $\text{Co}_{(1-x)}\text{Zn}_x\text{Fe}_2\text{O}_4$ ;  $x=0, 0.05, 0.1, 0.3$  and  $0.5$ ), with the same particle size distribution and amount of capping agent, was investigated. The X-Ray Power Diffraction (XPRD) measurements confirm the presence of pure cubic spinel phase in all samples; Rietveld refinement of the XPRD pattern indicated the increase of the lattice parameter with the increasing Zn content. Transmission Electron Microscopy (TEM) shows that the particles are sphere-like in shape with a mean diameter of  $5\pm 1$  nm. The amount of adsorbed oleic acid on the surface of the nanoparticles, determined by TG analysis, is around 25 %, indicating the formation of a complete monolayer on the surface of the nanoparticles. The presence of oleic acid on the surface of the nanoparticles and the nature of the bonding with the metal atoms on the surface of the NPs was confirmed by the FT-IR analysis. Also, a fingerprint region in FT-IR spectrum of metal–oxygen (Me–O, Me = Co, Fe, Zn) stretching modes of spinel ferrites was used to obtain information on the inorganic phase. By adding zinc in  $\text{CoFe}_2\text{O}_4$  structure the Me–O stretching mode of the octahedral and tetrahedral sites moved towards lower values, indicating a gradual substitution of cobalt ions by zinc ones. The change in a spinel structure was also confirmed by Raman spectroscopy. M vs H recorded at 5 K show a hysteretic behavior with decrease of coercive field with increase of zinc content. M vs T recorded by ZFC and FC protocols, indicates that all the samples are superparamagnetic at room temperature, while MZFC shows a maximum for all the samples with  $T_{\text{max}}$  decreasing with the increasing of Zn content. Mössbauer spectra has been recorded at low temperature (10 K) under an intense magnetic field (8T) in order to study the influence of Zn content on the magnetic structure. These measurements evidenced the modification of distribution of cations between interstitial sites with tetrahedral and octahedral symmetry.

Tuesday 3 July morning - 10:00/11:00

Parallel Session 2  
**METALLIC GLASSES III**  
Chair: K. Kelton

**ID-363 (Invited)****Atomistic details of ductility and structural relaxation from STZ Spectra**

*M. Atzmon<sup>1</sup>, L. Tianjiao<sup>1</sup>, L.R. DaCosta<sup>1</sup>, Y. Sun<sup>2</sup>, L. Greer<sup>3</sup>, W-H Wang<sup>4</sup>*

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<sup>4</sup> *Chinese Academy of Sciences*

In recent work, we have performed quasi-static measurements of anelastic relaxation in metallic glasses over >7 orders of magnitude in time. Conventional analysis of temporal data involves empirical fitting functions, which may easily lead to inconsistent results [1]. Instead, we computed relaxation-time spectra, which allow for a mechanistic analysis. For  $\text{Al}_{86.8}\text{Ni}_{3.7}\text{Y}_{9.5}$ , the spectra revealed an atomically-quantized hierarchy of shear transformation zones (STZs), with a distinct peak corresponding to each STZ size in a kinetic window corresponding to 14 to 22 atoms [2,3]. In the present work, we applied the same methodology to La-based alloys, some of which exhibit a high-frequency (beta) peak in dynamic-mechanical analysis. Since ductility correlates with a strong beta relaxation for varying compositions [4], this approach holds promise for an improved microscopic understanding of ductility. We observe two distinct regimes of STZ volume increment, consistent with differences in the roles of the alloying elements in plasticity. In addition, the size distribution of potential STZs provides a detailed atomic-scale description of structural relaxation beyond a single parameter.

[1] M. Atzmon, J. Appl. Phys. 123, 065103 (2018)

[2] J. D. Ju, D. Jang, A. Nwankpa and M. Atzmon, J. Appl. Phys., 109, 053522 (2011)

[3] J. D. Ju and M. Atzmon, Acta Mater. 74, 183 (2014)

[4] Z. G. Zhu, Y. Z. Li, Z. Wang, X. Q. Gao, P. Wen, H. Y. Bai, K. L. Ngai, and W. H. Wang, J. Chem. Phys. 141, 084506 (2014)

## ID-194

**Identifying the structural building blocks of metallic glasses using machine learning**

*J. Maldonis<sup>1</sup>, A.D. Banadaki<sup>2</sup>, S. Patala<sup>2</sup>, P.M. Voyles<sup>3</sup>*

<sup>1</sup> *University of Madison, Wisconsin*

<sup>2</sup> *North Carolina State University*

<sup>3</sup> *University of Wisconsin-Madison*

The structure of amorphous materials is complicated by their inherent disorder. For metallic glasses (MGs) in particular, this problem is compounded by high coordination numbers of local structural units, which dramatically increases the possible configurations that local short-range order (SRO) units can assume. Here we describe a new structure identification technique called motif extraction that learns structural motifs from atomic simulations of disordered materials using a new structure comparison metric called point-pattern matching (PPM) and machine learning clustering techniques.

In motif extraction, we first determine the similarity of each SRO unit, consisting of an atom and its nearest neighbors, to each other SRO unit in the simulated model using PPM. PPM removes trivial rotational and translational degrees of freedom to obtain a similarity score for each pair of SRO units, which is analogous to a “structural distance” between the two SRO units. The matrix of all the pair-wise similarity scores is amenable to machine learning clustering techniques. We use the clustering technique HDBSCAN to identify groups of SRO units with similar structure. Averaging the atomic positions around each atomic site generates a motif representative of the SRO units in the group. The set of motifs identified in this manner are the structural building blocks of the material.

We find twenty-four building-block motifs in a model of  $Zr_{50}Cu_{45}Al_5$  created by molecular dynamics (MD) quenching with an empirical potential. Some but not all of the motifs resemble close-packed local structures thought to be present in metallic glasses, such as Frank-Kasper polyhedra or icosahedra. The motifs form a recognizable progression with increasing coordination number, in which atoms are added to predictable sites to increase the coordination number. This progression raises the intriguing possibility of defining coordination defects in metallic glasses. The motifs also have some explanatory power for the properties and processes of the glass. The fraction of icosahedral motifs increases with temperature during cooling through the glass transition, and the glass has a high population of icosahedral and other close-packed motifs. Icosahedral motifs also exhibit chemical order, with a tendency to have Cu or Al central atoms. Two other motifs with coordination numbers 10 and 12 are more populous in the liquid state than in the glass.



**ID-200****Shear bands formation and plasticity of metallic glasses under laser shock peening**

*B. Wei*

*Key Laboratory of Microgravity (National Microgravity Laboratory), Institute of Mechanics, Chinese Academy of Sciences*

Bulk metallic glasses (BMGs), which possess many attractive properties including high strength, elastic deformability, and corrosion resistance, have attractive potential as structural materials. BMGs generally suffer from low ductility at ambient temperature, however, which limits their practical application. Shear bands (SBs) are preferential sites for further plastic flow due to structural and thermal softening. The unlimited propagation of localized SBs leads to catastrophic failure along a single SB. However, the nucleation and propagation of SBs is experimentally difficult to capture owing to the spatial and temporal confinements. In this work, the initiation of SB is studied using nanosecond laser shock peening (LSP) technique. The peening treatment produced an extra-deep shock-affected zone compared to crystal metal. As opposed to the conventional SBs, numerous arc SBs appeared and aggregated in the vertical direction of the laser beam, forming basic units for accommodating plastic deformation. The arc SBs exhibited short and discrete features near the surface of the material, and then grew longer and fewer at deeper peened layer depths, which was closely related to shock wave attenuation. An energy dissipation model was established based on Hugoniot Elastic Limit and shear band characteristics to represent the formation of an extra-deep shock-affected zone. The results presented here suggest that the bulk modification of metallic glass with a considerable affected depth is feasible. Further, they reveal that nanosecond laser peening is promising as an effective approach to tuning shear bands for improved MGs ductility.

**Tuesday 3 July morning - 10:00/11:00**

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY I**  
Chair: L. Da Monte

ID-387

## Engineered nanostructured thin films for thermionic-photovoltaic energy conversion at ultra-high temperatures

A. Bellucci<sup>1</sup>, M. Mastellone<sup>1</sup>, M. Girolami<sup>1</sup>, A. Generosi<sup>1</sup>, B. Paci<sup>1</sup>, A. Mezzi<sup>2</sup>, S. Kaciulis<sup>2</sup>, R. Polini<sup>3</sup>, S. Orlando<sup>1</sup>, V.Valentini<sup>1</sup>, D.M. Trucchi<sup>4</sup>

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<sup>4</sup> Consiglio Nazionale delle Ricerche

The H2020FET-OPEN project AMADEUS proposes the proof-of-concept of a novel solar thermal energy storage system based on phase change materials, such as pure silicon and boron with a high melting point (>1400 K) and a high latent heat capacity (10 times higher than the molten salts), combined with a solid-state energy conversion mechanism based on a hybrid thermionic-photovoltaic (TIPV) device. The TIPV cell, operating at very high temperatures (up to 2000 K) produces and exploits high electronic and photonic fluxes to convert heat directly and efficiently into electric power at very high power rates.

Specifically, our main aim is the development of low work-function thermionic electrodes able to manage a large current density at the operating temperatures. The thermionic cathode is under development with the deposition of thin films of nanostructured borides (lanthanum, cerium) grown on refractory substrates by nanosecond and femtosecond pulsed laser deposition and/or electron-beam evaporation. Single-crystal borides already demonstrated to be efficient thermionic emitters due to a low work function (typically <3 eV) and a high melting point (>2200 K). The challenge here is to extend these properties to low-cost large-area nano/micro-structured boride thin layers.

On the other hand, the anode of the TIPV converter is a thin layer deposited on a PV cell. The layer, which should have a work-function even lower than the cathode in order to collect the emitted electrons, must also be transparent to the blackbody radiation coming from the hot cathodic component thus allowing the PV cell to exploit this photon flux. Ultra-thin layers of alkali metal compounds (barium and cesium) are under development by electron-beam evaporation and magnetron sputtering as anodic coatings.

Grazing incidence x-ray diffraction, scanning-electron and atomic-force microscopies, Raman and x-ray photoelectron spectroscopies were used to investigate the chemical-physical properties of all the deposited thin films, allowing us to optimize their functional properties. Ultraviolet photoelectron spectroscopy and thermionic emission measurements were performed to evaluate the work-function and the operating temperature range of the emitting/collecting layers.

ID-182

**The influence of nonstoichiometry on the optical and catalytic properties of titania nanotubes**

*A. Valeeva*<sup>1,2</sup>, *I. Dorosheva*<sup>2</sup>, *A. Vokhmintsev*<sup>2</sup>, *R. Kamalov*<sup>2</sup>, *E. Kozlova*<sup>3</sup>, *D. Selishchev*<sup>3</sup>, *I. Weinstein*<sup>2</sup>, *A. Rempel*<sup>1,2</sup>

<sup>1</sup> Institute of Solid State Chemistry, Ural Branch, Russian Academy of Sciences

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<sup>3</sup> Borskov Institute of Catalysis, Siberian Branch, Russian Academy of Sciences

Nowadays design materials with given characteristics are widely used for creation materials with oriented structure and properties. The most promising possibility to modify the structure is changing of stoichiometry and inducing of structural vacancies. The aim of the present work is to consider in detail the growth of the 2D nanotubular titania film with nonstoichiometry near the interface with titanium foil and to study the influence of the nonstoichiometry on optical properties and photocatalytic activity under visible light of titania nanotubes depending of calcination temperature.

The nanotubular TiO<sub>2</sub> films with a nonstoichiometric layer near titanium foil were grown by anodization of Ti foil at a voltage of 20 V and time 15-360 min. An optimal anodization time to grow the ordered nanotubular TiO<sub>2</sub> film is 120 min, which allows one to achieve maximum length and effective area. The intense diffuse halo on XRD pattern clearly demonstrate that the anodized film has an amorphous nature. In the visible diffuse reflectance spectrum (ca. 490 nm) there is a broad dip of diffuse reflection, which is related to nonstoichiometry of amorphous TiO<sub>2</sub>. Calcination of films were performed at 200-600°C for 1 hour resulting in the changing of structure: amorphous titania transforms to anatase at about of 300°C and then anatase transforms to rutile at about 600°C.

The band gap width for nanotubular TiO<sub>2</sub> film anodized for 120 min is E<sub>g</sub> = 3.33 eV for indirect allowed transition. The analysis of DRS of the nanotubular TiO<sub>2</sub> films showed that the band gap width decreases from 3.53 to 3.23 eV at increasing of calcination temperature from 200 to 600°C.

The highest activity under visible light and under UV light as well, which is nearly one order of magnitude greater as compared to commercial TiO<sub>2</sub> (Degussa P25), was observed for nanotubular film annealed during 1 hour at 500°C, which consists of anatase titania phase. At higher temperatures, non-active rutile phase is formed resulting in the decrease in the acetone degradation rate. It should be noted that the photocatalytic activity of TiO<sub>2</sub> nanotubes under visible light was 3-4 times higher than in the case of commercial Degussa P25 and Kronos vlp7000. Nonstoichiometric titania nanotubes with specific vacancy defect structure can be considered as an active photocatalysts for the oxidation under visible light.

The study was financially supported by the Russian Foundation for Basic Research (Project No. 17- 03-00702).

ID-192

**ZnO-Fe<sub>2</sub>O<sub>3</sub> and ZnO-WO<sub>3</sub> nanoheterostructures: from synthesis to application in photoelectrochemical water splitting***D. Barreca<sup>1</sup>, A. Gasparotto<sup>2</sup>, C. Maccato<sup>2</sup>, C. Sada<sup>3</sup>, K. Kaunisto<sup>4,5</sup>, S. Bals<sup>6</sup>, T. Altantzis<sup>6</sup>*<sup>1</sup> CNR-ICMATE and INSTM, Department of Chemical Sciences, Padova University, 35131 Padova, Italy<sup>2</sup> Department of Chemical Sciences, Padova University and INSTM, 35131 Padova, Italy<sup>3</sup> Department of Physics and Astronomy, Padova University and INSTM, 35131 Padova, Italy<sup>4</sup> Department of Chemistry and Bioengineering, Tampere University of Technology, 33101 Tampere, Finland;<sup>5</sup> VTT Technical Research Centre of Finland Ltd, 33101 Tampere, Finland<sup>6</sup> EMAT, University of Antwerp, 2020 Antwerpen, Belgium

Photoelectrochemical (PEC) water splitting is a promising and sustainable technology for the production of solar fuels, such as clean hydrogen, from water and sunlight, largely available and in- exhaustible natural resources. Among the various metal oxides, ZnO, an n-type transparent semi- conductor with a high carrier mobility, has been extensively investigated as photoelectrode thanks to its low cost and non-toxicity. Nevertheless, actual bottlenecks for its utilization are represented by the wide band gap (3.3 eV), constraining light absorption to the UV interval, and by the rapid charge carrier recombination. To circumvent these obstacles, various efforts are being devoted to coupling of ZnO with other oxide semiconductors, in order to tailor their interfacial energetics to the target photoassisted process. In this context, the development of ZnO-Fe<sub>2</sub>O<sub>3</sub> and ZnO-WO<sub>3</sub> nanoheterostructures, in which ZnO nanosystems are functionalized with Fe<sub>2</sub>O<sub>3</sub> and WO<sub>3</sub>, provides an amenable route to master the system properties and compensate the single component disadvantages, leading to improved functional performances. In this work, ZnO-Fe<sub>2</sub>O<sub>3</sub> and ZnO-WO<sub>3</sub> nanocomposites were prepared by an original two-step vapor phase approach [1], consisting in the chemical vapor deposition of ZnO on fluorine-doped tin oxide (FTO) substrates, and in their subsequent functionalization with Fe<sub>2</sub>O<sub>3</sub> or WO<sub>3</sub> by means of radio frequency-sputtering. The developed systems were subjected to thermal treatment in air both before and after sputtering, and investigated in detail with particular regard to their structure, composition, morphology and optical absorption. The obtained results revealed the formation of highly porous ZnO nanostructures conformally covered by ultrathin  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (maghemite) or amorphous WO<sub>3</sub> overlayers. Functional tests for solar-driven photoelectrochemical water splitting evidenced a favourable performance enhancement with respect to bare ZnO, whose rationale lies in an improved separation of photogenerated charge carriers, enabled by the intimate contact between the two oxides. This achievement can be regarded as a valuable starting point for a future optimization of photoelectrodes for solar-assisted PEC water splitting, as well as for applications in other light-assisted processes, such as self-cleaning surfaces or air purification.

[1] D. Barreca et al., *Advanced Materials Interfaces*, 2017, 4, 1700161.

[2] D. Barreca et al., *CrystEngComm*, 2018, 20, 1282.

## ID 505

**A solution-processed tetra-alkoxylated zinc phthalocyanine as hole transporting material for perovskite solar cells**

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<sup>2</sup> Istituto per lo Studio dei Materiali Nanostrutturati (ISMN) - CNR, Via Salaria km 29.300, 00015 Monterotondo (Rm), Italy.

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<sup>4</sup> Ilse-Katz Institute for Nanoscale Science and Technology, Ben-Gurion University of the Negev, 84105 Be'er Sheva, Israel

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Perovskite solar cells have recently revolutionized the field of the emerging photovoltaic technologies. They have shown an impressive evolution in the last ten years, jumping from an initial 3.8% [1] to a 22.1% [2] certified efficiency but still have drawbacks to overcome, some of which are related to the use of the expensive Spiro-OMeTAD as hole transport material (HTM).

Phthalocyanines are macrocyclic aromatic compounds that possess excellent p-type semiconducting properties that make them appealing materials as hole transporters, and have recently scored cell efficiencies up to 17.5% [3] in perovskite-based devices. With the aim of obtaining an easily processable molecular material minimizing its synthetic pathway and optimizing its HOMO-LUMO values, we have synthesized a symmetrical tetra-n(butoxy)zinc phthalocyanine ((n-BuO)<sub>4</sub>ZnPc) in one synthetic step. The molecule can be solution-processed to form an effective and inexpensive hole-transport layer for perovskite solar cells. These appealing features are suggested by the results of a series of chemical, optical and voltammetric characterizations of the molecule, supported by the results of ab initio simulations. Preliminary measurements of (n-BuO)<sub>4</sub>ZnPc-methylammonium lead triiodide perovskite-based devices confirm such suggestion and indicate that the interface between the photoactive layer and the hole transporting layer is characterized by hole-extracting and electron-blocking properties, potentially competitive with those of other standards de facto in the field of organic hole-transport materials.

- [1] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. *J. Am. Chem. Soc.* 2009, 131(17), 6050-6051
- [2] Yang, W. S.; Park, B.-W.; Jung, E. H.; Jeon, N. J.; Kim, Y. C.; Lee, D. U.; Shin, S. S.; Seo, J.; Kim, E. K.; Noh, J. H.; Seok, S. I. *Science*, 2017, 356, 1376-1379.
- [3] Cho, K. T.; Trukhina, O.; Roldán-Carmona, C.; Ince, M.; Gratia, P.; Grancini, G.; Gao, P.; Marszałek, T.; Pisula, W.; Reddy, P. Y.; Torres, T.; Nazeeruddin, M. K. *Adv. Energy Mater.* 2017, 1601733.

**Tuesday 3 July morning - 10:00/11:00**

Parallel Session 4  
**POROUS MATERIALS I**  
Chair: G. Muscas



ID-179

**Nano-porous palladium used in hydrogen energy areas***X. Du<sup>1</sup>, L. Shao<sup>2</sup>, Z. Yang<sup>2</sup>, X. Ye<sup>1</sup>, C. Chen<sup>1</sup>**<sup>1</sup> Institute of Materials, China Academy of Engineering Physics**<sup>2</sup> Institute of Solid Mechanics, Beihang University*

Hydrogen energy, as a clean and renewable energy, has attracted more and more attentions today in the situation of global energy crisis. There are many researches on how to store and purify hydrogen isotopes. In the International Thermonuclear Experimental Reactor (ITER) project which is to establish an equipment to use hydrogen energy effectively, it's important to obtain the mixture of deuterium and tritium with a particular ratio. So we need to separate hydrogen isotopes with each other, and materials with excellent isotopes effect are needed.

In this work, Nano-porous palladium (np-Pd) with pore scale of about 5nm was fabricated by method of dealloying corrosion. This np-Pd has a huge specific surface area of above 150m<sup>2</sup>/g, which brings a great amount of reactive sites with hydrogen isotopes and shows high potential in hydrogen isotopes separation applications. The hydrogen isotopes absorption kinetic curves and pressure-composition isotherms (PCT) are used to study the isotopes effect of np-Pd. The hydrogen absorbing platform pressure is quite different from that of deuterium for all np-Pd samples, which makes it a promising separation material for hydrogen isotopes. We also carried out SEM and other characterizations to study the microstructure change of np-Pd after the hydrogen isotopes reaction experiments. Its helium immobilization properties are also to be studied. This work will help to promote the progress of ITER project.

## ID-190

**Functionalized nanoporous gold as a new biosensor for quantitative detection in ultra-low concentrations**

*P. Rizzi, F. Scaglione, E. Alladio, F. Turci, A. Damin, S. Bordiga, C. Giovannoli, L. Battezzati*

*Dipartimento di Chimica, Università di Torino*

The development of a new generation of ultra-sensitive sensors for analytical and bio-diagnostic devices requires a strong signal in front of a very small quantities of material. Taking advantage of peculiar plasmonic properties of nanoporous gold (NPG), a promising sensor for selective detection of Human Serum Albumin (HSA), as a proof of concept, has been prepared by a proper functionalization of the substrate.

NPG has been synthesized by chemical de-alloying an amorphous precursor,  $Au_{20}Cu_{48}Ag_7Pd_5Si_{20}$ , starting from melt spun ribbons. A fully de-alloyed ribbon with ligaments of around 60 nm was obtained after 4 h of de-alloying in proper conditions of temperature and concentration of the electrolyte. This material is self-standing and mechanical resistant and then well-versed for applications. At this stage, NPG is SERS active toward probe molecules (i.e. pyridine, bi-pyridine, rhodamine) even in very low concentration, but not specific for other complex molecule of interest such as HSA. Ad hoc functionalization is then required for this purpose.

Bare NPG has been bound with a selective ligand i.e. a target-directed antibody (anti-Human Serum Albumin, Ab anti-HSA) covalently grafted onto the gold surface and then tested by Surface Enhanced Raman Spectroscopy (SERS) measurements as a function of HSA concentration.

Data analyses in junction with a chemometric approach have successfully demonstrated that the NPG sensor is able to perform HSA quantitative detection in ultra-low concentrations.

ID-469

**Stimuli-responsive drug delivery systems based on mesoporous silica***V. Zelenak<sup>1</sup>, E. Benova<sup>2</sup>, M. Almasi<sup>2</sup>, A. Zelenakova<sup>3</sup>, V. Hornebecq<sup>4</sup>*<sup>1</sup> *Department of Inorganic Chemistry, University of P.J. Šafárik*<sup>2</sup> *Institute of Chemistry, Faculty of Science, P.J. Šafárik University, Košice, Slovakia*<sup>3</sup> *Institute of Physics, Faculty of Science, P.J. Šafárik University, Košice, Slovakia*<sup>4</sup> *3Aix Marseille University, CNRS, MADIREL, Marseille, France*

Drugs are essential components in human lives in terms of eliciting a therapeutic outcome in various disease states. However, high doses of the drugs can lead to side effects connected with the drug abuse. Particularly, drug molecules with lack of specificity and water solubility lead patients to take high doses of the drug to achieve sufficient therapeutic effects. The possible solution of these problems is to design biocompatible drug carriers that allow high loadings of drug molecules, including hydrophobic drugs, and their controlled release. Among the nanotechnology systems, recently intensively investigated as drug carriers belong periodic mesoporous silica materials. Mesoporous silica nanoparticles (MSN) represent a biocompatible multifunctional platform with favorable chemical properties. MSNs readily accommodate stimulus-responsive functionalization to enable on-command release of drug cargo in response to a variety of stimuli, including light, pH, temperature, magnetic field. They have shown better properties over free drug both in cell culture, and in animal models.

In our work we have studied a functionalized nanoporous silica particles responsive to the change of pH or UV radiation. In the first approach we have investigated MSN of MCM and SBA type modified by the photosensitive derivatives of coumarin and p-coumaric acid, which are subject of reversible photodimerization under UV radiation and create a “gate” on the surface. The obtained results showed the possibility of controlling of the pore accessibility and/or drug release from MSN by physical stimulus. Photodimerisation of p-coumaric acid (closing of pores) was faster than photodimerisation of coumarine.

In the second approach we studied pH-responsive platform consisting of cyclodextrin (CD)-capped MSNs. The pH-responsive nanovalves are composed of an amine-based stalk attached to the walls of silica nanoparticles that can bind beta-cyclodextrin units non-covalently through supramolecular interactions. When the pH is decreased from its initial value (pH=7.4), the amine derivatives become protonated and their binding affinity to the cyclodextrin drastically decreased. The cyclodextrin caps are thus dispersed and pores are un-blocked. In our studies nonsteroidal antiinflammatory drugs naproxen and indomethacin as model drugs were employed or we used an antineoplastic agent for the treatment of gastrointestinal cancers, 5-fluorouracil.

ID-464

**Silica nanosystems for active antifouling protection: nanocapsules and mesoporous nanoparticles in controlled release applications**L. Ruggiero<sup>1</sup>, A. Sodo<sup>1</sup>, F. Zurlo<sup>2</sup>, E. Di Bartolomeo<sup>2</sup>, A. Talone<sup>1,3</sup>, D. Peddis<sup>3</sup>, M.A. Ricci<sup>1</sup><sup>1</sup> Dipartimento di Scienze, Università degli Studi "Roma Tre"<sup>2</sup> Dipartimento di Scienze Chimiche e Tecnologie, Università degli Studi di Roma "Tor Vergata"<sup>3</sup> CNR - ISM

In several application fields, significant research efforts have been recently made to reduce the biocides environmental impact and to improve their effectiveness over time. This work reports the synthesis and the characterization of two different silica nanosystems dedicated to Cultural Heritage applications, based respectively on nanocapsules and mesoporous nanoparticles. Both these nanosystems, that will be part of a coating for stones conservation treatments, have been successfully loaded with a biologically-active compound: the 2-mercaptobenzothiazole (MBT). The loaded nanosystems have the aim of controlling the biocide release thus reducing the environmental impact. In fact, when the biocides are added into a coating formulation, the antifouling usually becomes quite short-lived, due to the premature release. As a consequence, this approach requires the use of very high concentrations of the biocide in order to maintain the antifouling function for long time. The encapsulation of biocides in nanosystems is a good way to reduce the amount of the biocide and to obtain a satisfactory long-action antifouling coating. The synthesis of nanocapsules is based on an encapsulation procedure: silica nanocontainers with core-shell structure have been synthesized by stabilizing condensation of tetraethyl orthosilicate TEOS through a dynamic self-assembly method. The diethyl ether was used as template and solvent for the MBT [1].

The mesoporous nanoparticles are synthesized by an incorporation procedure: mesoporous silica nanoparticles, obtained by the condensation of TEOS through a surfactant-assisted method [2], were used as scaffolds which immobilize MBT by physical adsorption after the synthesis.

Particle morphology (shape and size) was investigated by Scanning Electron Microscopy (SEM). In order to confirm the incorporation of MBT, Fourier transform infrared FTIR and Raman spectra were collected. To quantify the amount of the entrapped biocide, thermogravimetric tests were carried out. The controlled release of MBT from silica nanocontainers and silica scaffold dispersed in water was compared by UV-VIS spectrophotometry at different times.

The well known biocide effect of MBT makes the two developed nanomaterials a promising engineering system for multifunctional controlled release coating dedicated to outdoor cultural heritage surfaces.

[1] F. Maia et al.(2012), *Nanoscale*, 4, 1287–1298[2] N. Z. Knezevic et al.(2017), *MRS Advances*, 2 (19-20), 1037-1045

**Tuesday 3 July morning - 11:30/13:00**

Parallel Session 1  
**NANOSTRUCTURED MATERIALS IV**  
Chair: T. Sarkar

**ID-499 (Invited)****Demagnetizing-field corrections and packing-fraction distribution in magnetic nanoparticle assemblies**

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The measurement of the temperature dependence of dc and ac magnetization provides an indispensable tool to study magnetic nanoparticle assemblies, allowing the identification of supermagnetic transitions and single-particle features. The talk will highlight the importance of performing demagnetizing-field corrections on such curves. We recently demonstrated how demagnetizing-field effects can lead to shoulder peaks and other artifacts in such magnetization curves measured in dense assemblies [1]. As will be shown in the talk, these (otherwise misleading) features are successfully removed by the application of a straightforward correction method. More recently, it has been found that in thin (~ 20 micron) assemblies, unprecedented spin-glass-like cusps are revealed upon applying such corrections to ac curves. These results lead us to suggest that nanoparticle packing-fraction distribution can contribute to the smearing-out of collective magnetic features, and should be considered together with the (well-established) effects of particle-size distribution for a more complete analysis. Finally, results on a magnetic nanoparticle self-assembly will be presented, where the application of the correction method suggests the existence of a low-field anisotropy (additional to the shape anisotropy accounted for by the correction method) that occurs as a consequence of the ordered arrangement of the particles.

[1] P.S. Normile et al., Appl. Phys. Lett. 109, 152404 (2016)

ID-475

**Superspin glass and exchange bias behaviour of a dense assembly of ultra-small Mn ferrite nanoparticles: Monte Carlo simulations study***M. Vasilakaki<sup>1</sup>, G. Margaris<sup>1</sup>, D. Peddis<sup>2</sup>, R. Mathieu<sup>3</sup>, N. Yaacoub<sup>4</sup>, D. Fiorani<sup>2,5</sup>, K. Trohidou<sup>1</sup>*<sup>1</sup> *Institute of Nanoscience and Nanotechnology, NCSR "Demokritos,"*<sup>2</sup> *Istituto di Struttura della Materia-CNR*<sup>3</sup> *Department of Engineering Sciences, Uppsala University*<sup>4</sup> *LUNAM, Université du Maine, Institut des Molécules et Matériaux du Mans CNRS*<sup>5</sup> *Center of Nanomaterials Research, Immanuel Kant Baltic Federal University*

Magnetic behaviour of dense assembly of ultra-small ferrimagnetic nanoparticles exhibits unique features due to the combination of intraparticle and strong interparticle interactions [1]. A mesoscopic model has been developed for the particle assembly that describes efficiently the internal particle structure and the short- and long-range interparticle interactions [2]. The system exhibits exchange bias effect due to exchange coupling at the interface between core/surface spins and to the interparticle exchange coupling. Monte Carlo simulation technique with the implementation of the Metropolis algorithm has been performed to calculate the temperature dependence of the hysteresis and the zero-field-cooled/field-cooled magnetization. Our simulations reproduce well the experimental data of ultrasmall  $\sim 2$ -nm  $\text{MnFe}_2\text{O}_4$  nanoparticles, confirming the close relationship between the superspin glass state and the exchange-bias effect in dense nanoparticle systems, owing to the interplay between the intraparticle structure and the interparticle effects.

[1] D. Peddis, M. Vasilakaki, K. N. Trohidou, and D. Fiorani, *IEEE Trans. Magn.* 50, 2303304 (2014).

[2] M. Vasilakaki, G. Margaris, D. Peddis, R. Mathieu, N. Yaacoub, D. Fiorani, and K. N. Trohidou, *Phys. Rev. B* 97, 094413 (2018).

## ID-240

**In-situ XAS study of real-time Schlenk line synthesis hollow nanoparticles using synchrotron beam at the advanced photon source**

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<sup>2</sup> *Seoul National University*

<sup>3</sup> *Kennametal, Inc*

<sup>4</sup> *Argonne National Laboratory*

Recently, we have been successful in conducting in situ synchrotron quick-scanning X-Ray absorption spectroscopy (XAS) study of the synthesis of un-doped and doped hollow iron oxide nanoparticles (NPs) using Schlenk line set-up. Hollow iron oxide NPs have potential application in many fields: such as, as cancer treatment, drug delivery, Li ion batteries, etc. The  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> nanoparticles were synthesized by thermal decomposition of iron pentacarbonyl (Fe(CO)<sub>5</sub>). Analysis of in situ X-ray absorption near edge structure and extended X-ray absorption fine structure data, helped us to throw light on the real-time changes in the oxidation state and the chemical environment of the Fe atoms and the dopant (Mo, Co) atoms during the synthesis with time resolution of less than 1 min.

We observed few important phenomena in the kinetics of synthesis of iron oxide nanoparticles. The presence of the dopant precursor results in the accelerated decomposition of iron precursor and nucleation of Fe NPs. The atoms of the dopants are located at the surface of iron nanoparticles. The incorporation of the dopant atoms into iron oxide matrix occurred as a result of Kirkendall effect by which the inverse mass transport of Fe and O atoms internalizes dopant cations. Our results indicate a new mechanism of the doping process in metal oxide NPs. Such in-situ studies of chemical reactions will enable scientists and engineers to synthesize novel nanoparticles with tailor-made properties.



ID-412

**Tailoring the coercivity of Sm-Co-Cu thin films with variation of the copper content***M. de Campos<sup>1</sup>, S. Romero<sup>2</sup>, T. Germano<sup>2</sup>*<sup>1</sup> Federal Fluminense University<sup>2</sup> Physics Institute - University of Sao Paulo

Thin films of Sm-Co-Cu appear as possible alternative to PtCo and PtFe. Here, it is discussed the feasibility of Sm-Co-Cu thin films. In this study, targets of SmCo<sub>5</sub> and copper (99.8% purity) were employed. The deposition was performed by means of magnetron sputtering. The substrate was silicon single crystal, with orientation (100). The nominal temperature of deposition was 400°C.

A layer of chromium, with 50 nm of thickness was deposited on silicon substrate. Then a layer of SmCo<sub>5</sub> was deposited. Three subsequent different conditions were evaluated: (i) no addition of copper (ii) addition of small amount of copper (iii) addition of larger amount of copper. The thickness of the Sm-Co or Sm-Co-Cu layers is around 200 nm, as determined by Rutherford backscattering. A final layer of chromium, with 10 nm of thickness, was deposited in all three samples to avoid oxidation. It was found that the coercivity of sample (i) was 3.2 kOe. However, copper addition contributed to increase considerably the coercivity, that was 8.5 kOe for sample (ii) and 7.6 kOe for sample (iii). This shows that copper addition contributed for coercivity increase. It is possible that formation of rich copper phases, which may be paramagnetic, contributed to avoid magnetostatic interaction between Sm-Co phases, thus increasing coercivity. Similar feature was observed in Sm-CoFeCuZr magnets, where a magnetic insulating Sm(CoCu)<sub>5</sub> phase contributes to increase considerably the coercivity [1]. X-ray diffraction was performed and all the three samples have many different phases, ranging from stoichiometries 1:7 to 1:3. Among the present phases, are: 1:7 Sm(Co,Cu)<sub>7</sub>, 1:5 Sm(Co,Cu)<sub>5</sub>, 2:7 Sm<sub>2</sub>(Co,Cu)<sub>7</sub>, 5:19 Sm<sub>5</sub>(Co,Cu)<sub>19</sub>, 1:3 Sm(Co,Cu)<sub>3</sub>. Thus, the samples present significant inhomogeneity.

Summarizing, all the obtained hysteresis present good squareness, which is one of the main objectives of the magnetic recording industry. It was found that the coercivity of the samples can be controlled with the copper content, and this means that the process can be tailored to get a specific coercivity. The results indicate that the Sm-Co-Cu is promising as material for recording media. However, the inhomogeneity of the films may be a problem, because magnetic films cannot be heterogeneous for magnetic recording application.

[1] S. A. Romero et al. Journal of Alloys and Compounds 551 (2013) 312–317

ID-54

**Engineered Gd-Co based multilayer stack to enhanced magneto-caloric effect and relative cooling power**

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<sup>3</sup> *Materials and Nanomaterials Centre, Moroccan Foundation for Advanced Science, Innovation and Research, MAScIR, Rabat, Morocco*

Magnetic refrigeration based on the magneto-caloric effect is one of the best alternatives to compete with vapor-compression technology. The viability of a magnetic refrigeration system for magnetic cooling can be tested by exploiting materials in various forms, ranging from bulk to nanostructured materials. In order to achieve a wide refrigerating temperature range in magnetic refrigeration, we present in this study a 100 nm-thick Gd-Co alloys based multilayer stack. The stack is made of four individual Gd-Co alloy layers with different values of concentration and Curie temperature (TC). A magnetic entropy change associated with the second order magnetic phase transition was determined from the magnetic isotherms. Moreover, the relative cooling power of the studied Gd-Co based multilayer is enhanced compared to the one of bulk Gd, and reach a value of 200 J/kg as shown in Figure 1. This study demonstrates the potential of nanostructured Gd-Co multilayer stack for magnetic cooling applications.

Tuesday 3 July morning - 11:30/13:00

Parallel Session 2  
**METALLIC GLASSES IV**  
Chair: B. Sarac

ID-82

**Metallic glasses/composites prepared by powder metallurgy route and their mechanical properties***D. Wang**School of Materials Science and Engineering, Harbin Institute of Technology*

Ti-based bulk metallic glasses (BMGs) and diamond-reinforced composites were fabricated using spark plasma sintering technique. Compared with the as-cast and sintered BMGs, the composite exhibited enhanced hardness and fracture strength. Moreover, an inverse relation between the hardness and the tribological performance was noted, i.e. the sintered BMG had stronger wear resistance than the other samples for long distance sliding. The tribological mechanisms were further studied in detail and the results showed that the mechanical property of the BMG/composite could be designed and obtained for their engineering application by powder metallurgy method. On the other hand, diamond reinforced Al-based metallic glassy composites with high strength and improved plasticity were fabricated using a novel cold hydro-mechanical pressing (CHMP) of  $\text{Al}_{85}\text{Ni}_{10}\text{Ce}_5$  glassy/nanocrystalline powders. The glassy microstructure was retained after consolidation at room temperature and the strong bonding caused by severe deformation between the particles was responsible for excellent mechanical property of the bulk composites. Furthermore, an Al-based glassy alloy composite gear part was obtained due to the advantage of near-net-shape forming for CHMP. The experimental results suggest that Al-based metallic glasses/composites prepared by CHMP have engineering application potentials.

ID-110

## The evolution of ZrCu precipitation and mechanical properties improvement of the Zr-Cu-Al-Co bulk metallic glass composite by inoculating with Ta particles

*P. H. Tsai<sup>1</sup>, Y. C. Liao<sup>2</sup>, S. M. Song<sup>1</sup>, T. H. Li<sup>1</sup>, Y. L. Jian<sup>1</sup>, J. S. C. Jang<sup>1,2</sup>, J. C. Huang<sup>3,4</sup>*

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<sup>4</sup> Institute for Advanced Study; Department of Materials Science & Engineering, City University of Hong Kong

In some specified Zr-based alloy composition, it can precipitate ZrCu B2 phase from the amorphous matrix and form a bulk amorphous alloy composite (BAAC) by rapid solidification. When the ZrCu B2 phase subjected to the stress from the shear banding, it will absorb the energy of shear band and transform into ZrCu B19' phase, and results in improving the plasticity of Zr-based BAA. However, large agglomerated and inhomogeneous distributed ZrCu B2 phase usually occurred in the  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  BAA samples by conventional copper mold casting. Therefore, the concept of inoculation in conventional solidification process was applied to modify the size and distribution of ZrCu phase in this study. The Ta particles (size of 5–30  $\mu\text{m}$ ) with 0 ~ 1.0 vol.% were added into  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  BAA matrix as the inoculant. By using the characteristics of Ta, ultrahigh melting point (3290 K) and low solubility in Zr-base substrate, the Ta particles can act as the nucleation seeds for precipitating a homogeneously distributed ZrCu B2 phase in the matrix of  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  BAA. Moreover, the particle size of ZrCu B2 phase were further controlled by different cooling rates during solidification process. Based on the results of XRD analysis,  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  alloy rods with 0 ~ 0.75 vol.% Ta particle additions made by the copper mold at the temperature of  $-30^\circ\text{C}$  present amorphous structure co-existing with ZrCu B2 phase. However, when the temperature of copper mold increases to higher than  $-20^\circ\text{C}$ , the sample with 0.75 vol.% Ta particle additions will be totally crystallized. After adding Ta particles, the ZrCu B2 phase in the  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  alloy matrix exhibits round shape morphology and distributes more homogeneous. On contrary, when decreases the cooling rate of solidification, the large amount of ZrCu B2 phase will agglomerate into a large particle. The results of compression test reveal that the sample of  $Zr_{48}Cu_{47.5}Al_4Co_{0.5}$  BAAC with 0.75 vol.% Ta particle cast at  $-30^\circ\text{C}$  performs the significantly improved mechanical properties (1890 MPa fracture stress and 14% plastic strain) in comparison with the base BAAC (1560 MPa fracture strength and 7.5 plastic strain).

## ID-121

**Microstructure and mechanical properties of metallic nanoglasses prepared by nanoparticle consolidation**

*O. Adjaoud, K. Albe*

*Institute of Materials Science, Technische Universität Darmstadt*

Metallic nanoglasses are amorphous materials with microstructural features analogous to nanocrystalline materials, which consist of glassy grains connected by glass-glass interfaces. They can be produced by cold-compaction of glassy nanospheres which are prepared by inert-gas condensation [1,2]. The interfaces are characterized by an excess volume [3], a lack of short range order [4], and a different composition than the glassy grains [5,6]. In this contribution, we present a detailed analysis of microstructure formation of metallic nanoglasses by molecular dynamics simulations. Moreover, we discuss the thermodynamics and kinetic stability of nanoglasses, structural features of the interfaces, segregation effects and the mechanical response in uniaxial tensile tests. Finally, the computational results are put in the context of experimental findings.

[1] J. Jing et al., J. Non-Cryst. Solids 113, 167-170 (1989)

[2] J.X. Fang et al., Nano Lett. 12, 458-463 (2012)

[3] D. Şopu et al., Appl. Phys. Lett. 94, p. 191911 (2009)

[4] Y. Ritter et al., Acta Mater. 59, 6588-6593 (2011)

[5] O. Adjaoud et al., Acta Mater. 113, 284-292 (2016)

[6] O. Adjaoud et al., Acta Mater. 145, 322-330 (2018)

ID-334

## Atomic structure and mechanical behavior of amorphous TiNiCu alloy processed by severe plastic deformation

*A. Churakova*<sup>1,2,3</sup>, *E. Boltynjuk*<sup>2</sup>, *D. Gunderov*<sup>1,2,3</sup>, *E. Ubyivovk*<sup>2</sup>, *A. Kilmametov*<sup>4</sup>, *Y. Golovin*<sup>5,6</sup>, *A. Tyuri*<sup>5</sup>, *R. Valiev*<sup>1,2</sup>

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<sup>2</sup> Ufa State Aviation Technical University

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Melt-spun amorphous  $Ti_{50}Ni_{25}Cu_{25}$  ribbons were subjected to severe plastic deformation via high pressure torsion (HPT) at room temperature. Evolution of atomic structure was studied by means of TEM, AFM and density measurements. Changes in mechanical behavior were examined with help of tensile tests, fractography analysis and nanoindentation. TEM studies were performed on lamella-samples prepared in cross-section direction of HPT-processed specimens. HPT leads to a formation of high density of shear bands in homogeneous amorphous structure of initial amorphous  $Ti_{50}Ni_{25}Cu_{25}$  ribbons. Few nanocrystals form directly in the shear bands because of deformation-induced nanocrystallization. In regions close to shear bands formation of amorphous cluster-type structure was detected. Average size of clusters is 20 nm, they are observed in a region with a thickness of 200 nm near shear bands. At a distance of more than 200 nm from shear bands, the cluster-type contrast completely disappears, typical salt-pepper contrast is observed. AFM was used to study the surface morphology of foils prepared by ion polishing from the initial ribbons and HPT-processed specimens. Foils prepared from the initial ribbon have a smooth surface with an average roughness of 0.3 nm. In contrast, foils prepared from the HPT-processed specimens have holes with a depth of 2-4 nm and a width of 10-30 nm. The average width of holes is 10-30 nm which is close to the size of amorphous clusters observed in TEM. Density measurements demonstrate that HPT leads to a decrease in the density values by ~ 1.4% in comparison with the initial state, i.e. HPT leads to increase of free volume of amorphous  $Ti_{50}Ni_{25}Cu_{25}$  ribbons. The material in both initial state and after HPT processing demonstrates brittle fracture under uniaxial tensile testing at room temperature. However, changes in mechanical behavior of HPT-processed specimens in comparison with the initial ribbons were detected by means of nanoindentation and analysis of fracture surfaces. The observed drastic changes in structure and deformation behavior can be explained via the formation of a highly-heterogeneous amorphous structure as result of HPT processing.

**ID-346****FeCoNi(CrSi) high entropy alloy with good soft magnetic and mechanical properties***F. Li**School of Materials Science and Engineering, Zhengzhou University*

The high entropy alloy (HEA) FeCoNi(CrSi)<sub>0.4</sub> was synthesized by copper mold casting in this paper. Structure, thermostability, corrosion resistance magnetic and mechanical properties of the alloys in the states of as casting cold rolling and recrystallization annealing were investigated respectively. The research indicates that this HEA is very stable to deformation and heating due to the formation of simple face centered cubic structure. Moreover, this alloy shows high saturated magnetization ( $B_s$ ) nearing 120 emu/g and good tensile ductility. This HEA also exhibits much better soft magnetic properties low coercivity ( $H_c$ ) of 73 A/m than that of the current HEAs reported to date. The unique combination of magnetic and mechanical properties of the HEA suggest a good application prospect.



## ID-243

**Tensile creep and physical mechanism in  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  and  $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$  metallic glasses.**

J. Qiao<sup>1</sup>, J.M. Pelletier<sup>2</sup>, Y. Yao<sup>1</sup>

<sup>1</sup> School of Mechanics, Civil Engineering and Architecture, Northwestern Polytechnical University, Xi'an 710072, P.R. China

<sup>2</sup> MATEIS, INSA-Lyon

As a relatively new family of amorphous materials, metallic glasses are attractive since they exhibit excellent mechanical properties. Among these properties, the elastic strain, the yield stress and the stress to failure are the more interesting ones. These properties are usually measured at room temperature. When the temperature increases, these features evolve drastically: viscoplasticity occurs and the possibility of large deformation is observed but the mechanical strength decreases strongly. In addition to pure tensile or compressive tests, creep experiments are also possible and give a lot of information on the behavior of the material when a constant stress is applied, for instance during thermoforming.

The present work addresses the creep behavior during tensile deformation in two metallic glasses:  $\text{Cu}_{46}\text{Zr}_{46}\text{Al}_8$  and  $\text{La}_{60}\text{Ni}_{15}\text{Al}_{25}$ . Both temperature and stress level have been changed in a large range. Behavior during unloading has also been investigated. When temperature and/or stress increase a transition from a linear to a non-linear response is observed, i.e. that the compliance (the ratio between stress and strain) becomes stress dependent. This transition indicates the increase in the magnitude of the viscoplastic component.

A physical model is presented to describe these curves, based on the concept of defect, which evolve as a function of stress and temperature.

Tuesday 3 July morning - 11:30/13:00

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY II**  
Chair: S. Fabbrici

**ID-492 (Invited)****Thermomagnetic phase transitions and magnetocaloric materials**

*V. Franco, A. Conde, J.Y. Law J.Y.*

*Dpto. Física de la Materia Condensada, ICMSE-CSIC, Universidad de Sevilla*

From the Materials Science point of view, the magnetocaloric effect (MCE), i.e. the reversible temperature change of a magnetic material upon the application/removal of a magnetic field, has both technological importance related to its application for efficient energy conversion, as well as fundamental interest for the study of thermomagnetic phase transitions. While MCE materials with a first order phase transition exhibit sharper and narrower MCE peaks than second order phase transitions, this is at the expense, in most of the cases, of thermal and magnetic hysteresis, which limit the applicability of first order phase transition materials for cyclic operation [1].

In this talk we will show that magnetocaloric characterization can be useful to quantitatively determine the order of thermomagnetic phase transitions in a broad variety of materials [2]. We will also demonstrate that the composition separating FOPT and SOPT of a series of alloys can be quantitatively determined by taking into account the field dependence of the magnetic entropy change [3] and that temperature first order reversal curves (T-FORC) can be used to characterize the hysteresis of magnetocaloric materials [4]. These results will be illustrated with examples of different families of first order phase transition alloys and compounds.

Supported by AEI/FEDER-UE (project MAT-2016-77265-R) and the PAI of the Regional Government of Andalucía.

[1] V. Franco, J. S. Blazquez, J. Ipus, J. Y. Law, L. M. Moreno-Ramirez, A. Conde, "Magnetocaloric effect: from materials research to refrigeration devices", *Progress in Materials Science* 29, 112-232 (2018).

[2] J. Y. Law, V. Franco, L.M. Moreno-Ramírez, A. Conde, D. Y. Karpenkov, I. Radulov, K. P. Skokov, and O. Gutfleisch, "New quantitative criterion for determining the order of thermomagnetic phase transitions based on magnetocaloric effect". *Nature Communications* 2018 (to be published).

[3] V. Franco, J.Y. Law, A. Conde, V. Bravander, D. Y. Karpenkov, I. Radulov, K. Skokov, and O. Gutfleisch, "Predicting the tricritical point composition of a series of LaFeSi magnetocaloric alloys via universal scaling", *J. Phys D: Appl. Phys.* 50, 414004 (2017).

[4] V. Franco, T. Gottschall, K. P. Skokov, and O. Gutfleisch, "First-Order Reversal Curve (FORC) Analysis of Magnetocaloric Heusler-Type Alloys", *IEEE Magnetics Letters* 7, 6602904 (2016).

ID-67

## Assessing two rapid quenching techniques for the production of magnetocaloric alloys

G. Potnis<sup>1</sup>, J. Das<sup>1</sup>, M. Krautz<sup>2</sup>, A. Gebert<sup>3</sup>, A. Waske<sup>2</sup>, J. Eckert<sup>4</sup>

<sup>1</sup>Department of Metallurgical and Materials Engineering, Indian Institute of Technology Kharagpur

<sup>2</sup>Leibniz Institute for Solid State and Materials Research

<sup>3</sup>IFW Dresden

<sup>4</sup>Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria

Room-temperature magnetic cooling has progressed towards application during the last decade. La-Fe-Si based materials are considered as potential candidates to replace the current benchmark material Gadolinium. In comparison to the chemically pure element, only the  $\text{NaZn}_{13}$ -type structure in the La-Fe-Si-based materials exhibits a large magnetocaloric effect. After casting La-rich phases and  $\alpha$ -Fe are present. The magnetocaloric  $\text{NaZn}_{13}$ -phase, however, is only stable at elevated temperatures, around 1300K, i.e. heat treatment after casting is required. Commonly, La-Fe-Si-based materials are casted by conventional techniques, such as arc melting or induction melting, resulting in a microstructure with relatively inhomogeneous phase distribution. It also has been reported recently, that melt spinning in ternary La-Fe-Si alloys leads to a refined microstructure, reducing the annealing time to only several hours [1]. For room-temperature application, ternary alloys are not feasible, since they exhibit the large magnetocaloric effect only well-below room temperature. In contrary, Mn-doping and subsequent hydrogenation adjusts the materials working temperature to room-temperature [2]. Since Mn-destabilises the  $\text{NaZn}_{13}$ -type structure, annealing parameters have to be adjusted in comparison to the ternary alloys. In our study, we compare a Mn-doped La-Fe-Si-based alloy,  $\text{LaFe}_{11.4}\text{Mn}_{0.2}\text{Si}_{1.2}$ , casted by three different techniques leading to different microstructures. We used arc-melting, suction casting and melt-spinning in order to compare the influence of phase distribution in the microstructure on the annealing time required to obtain almost single-phase magnetocaloric  $\text{NaZn}_{13}$ -phase. By X-ray diffraction and electron microscopy, the microstructure and phase constitution of the as-cast and annealed samples are reported. The magnetocaloric effect is assessed by magnetic measurements. We show, that rapid quenching techniques, like suction casting and melt-spinning lead to a significant reduction of the required annealing time from 7 days to only 3 or 1 day, respectively. In contrast to conventional bulk materials, suction cast cylinders and melt spun ribbons represent convenient shapes for implementation as magnetocaloric regenerators.

[1] X.B. Liu et al., J. Phys. Condens. Matter. 16 (2004) 8043–8051. doi:10.1088/0953-8984/16/45/026.

[2] M. Krautz et al., J. Alloys Compd. 598 (2014) 27–32. doi:10.1016/j.jallcom.2014.02.015.

## ID-126

**Experimental study of Curie temperature distributions on mechanically alloyed Fe<sub>70</sub>Zr<sub>30</sub> systems: effect on magnetocaloric response and magnetic properties**

*A.F. Manchón-Gordón, J.J. Ipús, L.M. Moreno-Ramírez, J.S. Blázquez, C.F. Conde, V. Franco, A. Conde*

*Universidad de Sevilla*

Several aspects inherent to powder samples of amorphous alloys obtained by ball milling technique affect their magnetic response. For example, in the case of the magnetocaloric effect, a general decrease of the peak value and a large broadening of the thermal dependence of the magnetic entropy change are observed due to the presence of inhomogeneities in the amorphous matrix. These inhomogeneities lead to the existence of a non-negligible distribution of Curie temperatures. In this work, amorphous alloys with Fe<sub>70</sub>Zr<sub>30</sub> composition were prepared by ball milling. The evolution of magnetocaloric response and temperature dependence of magnetic properties has been analyzed. The distribution of Curie temperatures was obtained by two independent techniques: a) from the temperature dependence of the hysteresis loops, applying the law of approach to saturation to determine the saturation magnetization, and b) studying the local environment of Fe atoms from Mössbauer spectrometry. A good agreement is found assuming a Gaussian distribution of Brillouin's functions to describe the experimental results.

**Acknowledgements**

This work was supported by AEI/FEDER-UE (Project MAT-2016-77265-R) and the PAI of the Regional Government of Andalucía. A.F. Manchón-Gordón acknowledges a fellowship from the University of Sevilla. L.M. Moreno-Ramírez acknowledges a FPU fellowship from the Spanish MECD.

ID-383

**Influence of atomic disorder on the ground state of Ni-Co-Mn-Sn alloys with regular and inverse Heusler structures: ab initio study***V. Buchelnikov<sup>1</sup>, V. Sokolovskiy<sup>1</sup>, M. Zagrebin<sup>1</sup>, B. Barbiellini<sup>2</sup>, O. Miroshkina<sup>1</sup>*<sup>1</sup>*Chelyabinsk State University, Chelyabinsk, Russia*<sup>2</sup>*Lappeenranta University of Technology, Lappeenranta, Finland*

Co-doped Ni-Mn-Sn shape memory alloys have drawn a lot of attention in recent years. The Co-doping leads to a decrease in both the martensitic transformation temperature and Curie temperature of martensite and to an increase in the Curie temperature of austenite. Besides, the large change in a magnetization in the vicinity of structural transformation can occur. As a result, the tuning of Co and Mn contents can achieve the better magnetocaloric properties [1].

In this work, we focus on the effect of atomic disorder on the structural, magnetic and electronic properties of Ni-Co-Mn-Sn systems by using ab initio calculations, which were based on the density functional theory implemented in the VASP (The Vienna Ab initio Simulation Package) [2, 3] and SPR-KKR (A spin polarized relativistic Korringa-Kohn-Rostoker code) packages [4] within the 32-atom supercell and coherent potential approximation, respectively. The ground state calculations were performed for two compositions (Ni<sub>13</sub>Co<sub>3</sub>Mn<sub>13</sub>Sn<sub>3</sub> (regular Cu<sub>2</sub>MnAl-type: \#225) and Mn<sub>13</sub>Co<sub>3</sub>Ni<sub>13</sub>Sn<sub>3</sub> (inverse Hg<sub>2</sub>CuTi-type: \#216). It should be noted that the optimized atomic positions for compositions studied were obtained by the US-PEX (Universal Structure Predictor: Evolutionary Xtallography) package [5]. With respect to the exchange-correlation potential, a series of ground state calculations were performed using both the GGA-PBE functional and Meta-GGA with SCAN functional [6].

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ID-426

**Development of Fe-rich soft magnetic metallic glass matrix composite utilizing nucleation seed***K.J. Kim, K.N. Yoon, W. Kim, E.S. Park**Seoul National University*

With regard to the recent energy crisis, magnetic core loss ( $W$ ) properties have begun to attract attention in order to minimize the energy loss of transformer during power generation. For these reasons, Fe-based amorphous/nanocrystalline composite alloys with low coercivity ( $H_c$ ) have been mainly developed, which is produced by annealing the amorphous phase while limiting the Fe content and precipitating BCC  $\alpha$ -Fe nano-crystallites. However, there is no clear solution yet to overcome magnetization-coercivity trade off. In the present study, we developed Fe-rich soft magnetic amorphous/nanocrystalline composite utilizing nucleation seed of  $\alpha$ -Fe clusters to achieve relatively high saturation magnetization ( $M_s$ ) as well as low core loss. Fe-based ribbon alloys were produced through a series of procedure including induction melting, arc melting and melt spinning process. Glass-forming region in Fe-rich composition and structures in as-quenched and annealed states were identified by x-ray diffractometry (XRD). Simultaneously, we evaluated thermal property such as glass transition temperature ( $T_g$ ), crystallization onset temperature ( $T_x$ ) and super-cooled liquid region ( $\Delta T_x$ ) by differential scanning calorimetry (DSC). Finally, we measured hysteresis loop, magnetic properties such as saturation magnetization and coercivity, and permeability of as-quenched and annealed samples by vibrating sample magnetometry (VSM). As a result, homogeneous and large volume fraction (vf. %) of BCC  $\alpha$ -Fe nano-crystallites were precipitated through designing high Fe content and utilizing nucleation seed of  $\alpha$ -Fe clusters formed during rapid cooling. We developed a highly efficient Fe-based soft magnetic metallic glass composite with higher saturation magnetization than 1.5T as well as lower coercivity than 15A/m, which enables minimization of the energy loss of the soft magnetic material transformer. This study provides a meaningful guideline on how to control microstructure and related properties in Fe-based soft magnetic metallic glass composite.

Keyword: Fe-rich metallic glass,  $\alpha$ -Fe cluster, nanocrystalline composite, high saturation magnetization, lower coercivity

Tuesday 3 July morning - 11:30/12:45

Parallel Session 4  
**POROUS MATERIALS II**  
Chair: M. Ferretti



**ID-249****Wollastonite: synthesis and additive manufacturing of porous-controlled scaffolds**

*M.C. Luna<sup>1</sup>, M. Horynová<sup>1</sup>, E.B. Montúfar<sup>1</sup>, J. Rodríguez<sup>2</sup>, L. Celko<sup>1</sup>*

<sup>1</sup> Central European Institute of Technology - Brno University of Technology

<sup>2</sup> Central European Institute of Technology

Wollastonite is a calcium silicate that is gaining attention due to its attractive properties that suit in a wide range of applications for different industries that go from thermal insulation, absorption of metallic ions in catalysis, filters and water purification, reinforcement phase in composites, and most recently as a bioactive material. The additive manufacturing technique has been used for the production of diverse shaped structures with different degrees and amount of open porosity made of wollastonite, mainly for its use in orthopedics. The aim of the present work is to establish an easy synthesis and processing of wollastonite powder to elaborate porous structures via robocasting. An injectable paste that serves as an ink was developed to build up an in-silico designed cylindrical structure of 10 mm in diameter and 10 mm in height. Using a tip of 410  $\mu\text{m}$ , the cylinders were 3D- printed following two different arrangement patterns, named as honeycomb and rectilinear infills. In the same way, two pore sizes of 350 and 500  $\mu\text{m}$  were produced. The final structures were evaluated in terms of their porosity, arrange, shape and size of pores by X-ray diffraction, scanning electron microscopy and compression test. The final consolidated porous scaffolds represent a novel material suitable for a wide range of applications.

ID-341

**Silica aerogels – fabrication, properties and overcoating with diamond thin film***J. Torres-Rodríguez<sup>1</sup>, M. Varga<sup>2</sup>, A. Kromka<sup>3</sup>, E.B. Montúfar<sup>1</sup>, I. Lázár<sup>4</sup>, J. Kalmár<sup>4</sup>, K. Dvořák<sup>5</sup>, L. Celko<sup>1</sup>*<sup>1</sup> *Central European Institute of Technology - Brno University of Technology*<sup>2</sup> *Institute of Physics, Czech Academy of Sciences*<sup>3</sup> *Institute of Physics of the ASCR*<sup>4</sup> *Department of Inorganic and Analytical Chemistry, University of Debrecen*<sup>5</sup> *Brno University of Technology, Faculty of Civil Engineering*

Silica aerogels are lightweight and highly porous materials, formed by a three-dimensional inter-connected network of nanoparticles, which possesses outstanding properties such as low thermal conductivity and density. Hence, including other applications, silica aerogels can be applied as thermal insulator, Cerenkov radiation detectors, adsorption and catalyst supports. In exploring new opportunities has been found that deposition of carbon layers can help to improve among others, the mechanical and electrical properties of the aerogels. In this work, we tested the feasibility to produce diamond thin films on highly porous SiO<sub>2</sub> aerogels. Due to the open pore structure, high porosity and large surface area of aerogels, make them promising candidates as starting porous medium for preparing composite materials using chemical vapor infiltration techniques. Here, we firstly prepared monolithic SiO<sub>2</sub> aerogels by sol-gel method and subsequent low temperature supercritical drying. Then, thin diamond films were grown onto the dried aerogels using a microwave plasma enhanced chemical vapor deposition system. The film quality and surface morphology were characterized by Raman spectroscopy and scanning electron microscopy respectively. The effect of the deposited layer on the surface area and porosity of the aerogels were also studied.

## ID-43

**Behavior of cementitious materials with mineral additions towards the transport of ionic species: application to electrokinetic remediation processes**

*I. Martínez, M. Castellote*

*IETcc-CSIC*

Concrete industry is blamed to contribute global CO<sub>2</sub> gas emission into atmosphere between 5% and 7% due to the use of OPC in the production of concrete. Worldwide there is an overwhelming consensus in concrete industry to reduce the carbon footprint of concrete through reducing the bulk portion of cement in the concrete. The use of supplementary cementitious materials, SCMs, is a common practice now-a-days. Pozzolanic materials such as silica fume (SF), fly ash (FA) and granulated blast furnace slag (GGBFS) are commonly used due to unique characteristics of each material in improving the properties of cement concrete.

The incorporation of mineral admixtures as SCMs can prolong the service life of a structure and contribute to its mechanical properties by decreasing the permeability of a material, which reduces the entry of aggressive agents from the environment. Despite the benefits of incorporating mineral admixtures in concrete, studies have indicated that blending of SCMs with Portland cement leads to a more complicated system where the hydration of the Portland cement and hydraulic reaction of the SCM occur simultaneously. The reaction of most SCMs is slower than the reaction of the clinker phases and depends on the chemical composition, the fineness, and on the amounts of reactive phases.

Corrosion of the reinforcing steel is caused by presence of aggressive substances in the interior of concrete that provoke a decrease in the pH of the pore solution. The penetration of chlorides from the environment is one of the most important causes of corrosions, that's why chloride migration, its combination with the cement phases as well as the critical chloride content that cause steel depassivation, have been highly studied. In this field, the determination of the chloride diffusion coefficients has been an important advance to predict the deterioration establishing the model of the process.

Even though the influence of different mineral additions in the chloride combination and the diffusion coefficients of chlorides through concrete has been discussed by the scientific community, the effects of mineral admixtures on electrokinetic remediation processes have not been investigated in depth. From this viewpoint, in this work the influences of SF, FA and GGBFS on the transport of chloride through the pore structure have been evaluated, leading to conclusions in the viability of the application of electrochemical chloride treatments in these materials.

## ID-96

**Three-dimensional bicontinuous nanoporous materials by vapor phase dealloying**

Z. Lu<sup>1</sup>, P. Liu<sup>2</sup>, A. Hirata<sup>1</sup>, J. Erlebacher<sup>3</sup>, M. Chen<sup>3</sup>, J. Han<sup>4</sup>

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Three-dimensional bicontinuous open (3DBO) nanoporosity has been recognized as an important nanoarchitecture for catalysis, sensing, and energy storage. Dealloying, i.e., selectively removing a component from an alloy, is an efficient way to fabricate nanoporous materials. However, electrochemical and liquid-metal dealloying methods can only be applied to a limited number of alloys and usually require an etching process with chemical wastes. Here, we developed a vapor-phase dealloying (VPD) method by utilizing the vapor pressure difference between solid elements to selectively evaporate a component from an alloy. This method can be applied to a variety of elements from less-noble metals to inorganic elements regardless of their chemical, and electrochemical activity and electric conductivity. The elements with low melting point can also be fabricated using a low dealloying temperature by reducing dealloying pressures. Importantly, the sublimated elements can be fully recovered and do not cause any environmental issues. This environmentally friendly and highly efficient dealloying method paves a new way to fabricate and design bicontinuous nanoporous materials for a wide range of structural and functional applications.

## ID-204

**Using a unique complex surface treatment, sand-blasting/acid-etching/alkaline-immersion, to enhance the corrosion resistance and biological responses of titanium surface**

*Y-S Sun<sup>1</sup>, H-H Kao<sup>2</sup>, H-H Huang<sup>1</sup>*

<sup>1</sup> *Department of Dentistry, National Yang-Ming University, Taiwan*

<sup>2</sup> *Institute of Oral Biology, National Yang-Ming University, Taiwan*

Titanium (Ti) has been widely used as dental and orthopedic implant due to its good mechanical properties and biocompatibility. The bioinert surface and dense metallic substrate of Ti implants only provide an interfacial connection with surrounding bone, instead of an aggressive bone ingrowth. Besides, there are some clinical cases showing that the Ti ions may result in biological side effects. Therefore, developing a porous Ti implant surface with bioactive and corrosion resistant characters is expected to improve the long-term clinical success. In this study, we chose a complex surface treatment, sand-blasting/acid-etching/alkaline-immersion, to further decrease the Ti ions release and meanwhile increase the surface bioactivity and biological responses. The results showed that a hybrid oxide layer was formed on the surface-modified Ti, containing an interconnected porous TiO<sub>2</sub> outer layer (pore size 50-500 nm; thickness 150-200 nm) and an amorphous-like dense TiO<sub>2</sub> inner layer (thickness 50-100 nm). The corrosion resistance of surface-modified Ti surface was increased due to the presence of dense inner layer. As compared with the dense metallic substrate on the untreated Ti surface, the porous outer layer on the surface-modified Ti surface was more hydrophilic and bioactive, and adsorbed higher protein albumin. This led to a further improvement in the adhesion, proliferation, and mineralization of human bone marrow mesenchymal stem cells. We conclude that the proposed unique complex surface treatment has high potential in dental and orthopedic implant applications.

**Keywords:** Titanium implant; Surface treatment; Porous oxide layer; Corrosion resistance; Biological response.

**KEYNOTE LECTURE**

Chair: M. Farle

**Combinatorial and high-throughput methods for the investigation of novel materials**

A. Ludwig

*Institute for Materials, Ruhr-University Bochum, Bochum, Germany*

The design of new materials is a key challenge in materials science: e.g. new nanostructured materials for the sustainable production/storage/conversion of energy carriers are necessary to improve existing and to enable future energy systems. Efficient methods for discovery and optimization of new materials are necessary. By implementing and optimizing the thin-film combinatorial materials science approach in our group for >10 years, we are trying to contribute to this development. It comprises the fabrication and processing of thin film materials libraries by combinatorial sputter deposition processes (40 elements available) and optional post-deposition treatments (e.g. thermal oxidation, annealing, dealloying), followed by the high-throughput characterization of the different thin film samples contained in these libraries. The importance of defining adequate screening parameters and the according design of different materials libraries suitable for one or more screening parameters will be addressed. Our high-throughput material characterization methods are automated, fast, and mostly non-destructive: examples are EDX and RBS for composition, XRD for crystal structure, temperature-dependent resistance for phase transformation, high-throughput test stands for optical properties (color, transmission) and mechanical properties (stress, hardness, elastic modulus), and scanning droplet cells for photoelectrochemical properties screening. The obtained results for up to quinary systems are visualized in the form of composition-processing-structure-function diagrams, interlinking compositional data with structural and functional properties. The talk will cover and discuss examples of the combinatorial development of nanoscale materials with a focus on the combinatorial synthesis of multinary nanoparticle libraries by combinatorial sputtering into ionic liquids. Further examples include nanoscale shape memory alloys, multiple principal element alloys and metal oxide thin film materials libraries for solar water splitting.

Tuesday 3 July afternoon - 15:30/17:00

Parallel Session 1  
**NANOSTRUCTURED MATERIALS V**  
Chair: B.S. Murthy

**ID-498 (Invited)****Reversible sodium and lithium insertion in iron fluorides**

M-L Doublet<sup>1</sup>, E. Kemnitz<sup>2</sup>, N. Pinna<sup>2</sup>

<sup>1</sup> Institut Charles Gerhardt, CNRS UMR5253, Université Montpellier, France; Réseau Français sur le Stockage Elec-trochimique de l'Energie, Amiens, France

<sup>2</sup> Institut für Chemie and IRIS Adlershof, Humboldt-Universität zu Berlin, Germany

Li-ion batteries (LIBs) are omnipresent in consumer electronics and are seen as the most promising technology for electric vehicles. Na-ion batteries (NIBs) have emerged as viable and cheaper alternatives for stationary applications where Li-ion batteries are too expensive. However, the larger size of sodium ion compared to lithium makes traditional positive materials for LIBs not always suitable for the reversible insertion of sodium ions.

3d-transition metal fluorides, such as  $\text{FeF}_3$ , have drawn attention as NIBs and LIBs positive electrode material due to their ability to deliver high potential thanks to the high polarity of the metal-fluorine bond. However, the insulating character of these highly ionic materials in practice leads to high polarisation and slow insertion kinetics [1-3]. Moreover, since the positive electrode in current LIBs and NIBs is the reservoir of alkali ions, metal fluorides are not applicable in alkali-ion technology against a carbonaceous anode without pre-lithiation/sodiation [1].

Therefore in order to solve these problems, here we introduce a microwave-assisted solution synthesis of  $\text{NaFeF}_3$  perovskite nanoparticles from pre-synthesized rutile  $\text{FeF}_2$  colloidal particles, sodium ethoxide and ammonium fluoride is presented. This  $\text{NaFeF}_3$  material shows a reversible electrochemical activity of 1Na or 1Li per iron with low polarisation and excellent capacity retention after 100 cycles. The unexpected reversible insertion of both sodium and lithium ions, studied through ex-situ and operando X-ray diffraction measurements, is attributed to a kinetic stabilization of corner-shared cubic  $\text{A}_x\text{FeF}_3$  ( $\text{A} = \text{Li}, \text{Na}$ ) frameworks along the cycles involving low volume change without high thermodynamic cost as supported by a polymorphism theoretical analysis [3].

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## ID-40

**BN/Ag nanohybrids with enhanced catalytic activity**

*A. Konpatsky<sup>1</sup>, K. Firestein<sup>2</sup>, D. Leybo<sup>1</sup>, A. Steinman<sup>1</sup>, A. Kovalskii<sup>1</sup>, A. Matveev<sup>1</sup>, A. Manakhov<sup>1</sup>, D. Golberg<sup>2</sup>, D. Shtansky<sup>1</sup>*

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<sup>2</sup>School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), Brisbane, Queensland 4000, Australia.

Nanohybrid materials consisting of hexagonal boron nitride nanoparticles (BNNPs) and Ag nanoparticles (AgNPs) (hereafter denoted as BNNPs/Ag) were fabricated. Dependence of the BNNPs/Ag catalytic activity on the boron oxide ( $B_2O_3$ ) content on the surface of BNNPs was investigated. BNNPs with different amount of  $B_2O_3$  on their surface were prepared during air annealing at 1100 for 1, 5, 10 min. BNNPs that were not subjected to air annealing were used as reference samples. In order to evaluate changes in  $B_2O_3$  content versus annealing time, TGA analysis imitating air annealing was conducted. AgNPs were deposited on the surfaces of BNNPs via  $AgNO_3$  decomposition under UV irradiation. HR-TEM and STEM data demonstrated that AgNPs size distribution was rather narrow (5-10 nm). TEM and XPS results showed that the highest amount of Ag was in case of BNNPs/Ag sample with moderate amount of  $B_2O_3$  on their surfaces (5 min air annealing). Chemical state of AgNPs on the surfaces of BNNPs was investigated by XPS analysis. The results indicated that Ag does not form a detectible amount of oxide and can be well fitted using only one peak corresponding to metallic Ag. Catalytic performance of the BNNPs/Ag nanohybrids was investigated for methanol oxidation reaction. Temperature of full methanol conversion was used to characterize catalytic activity of the BNNPs/Ag. It was demonstrated that the catalytic activity linearly rises with increasing annealing time in air up to 5 min and significantly drops in case of samples subjected to 10 min air annealing. These results correlate well with Ag content data obtained for all samples and indicate that an excessive amount of  $B_2O_3$  is not beneficial for catalytic performance, whereas the optimal amount of  $B_2O_3$  on the surfaces of BNNPs leads to considerable enhancing of BNNPs/Ag nanohybrid catalytic activity.

ID-233

## Synthesis and characterization of Sn reinforced Al-Cu-Fe quasicrystalline matrix nanocomposite by mechanical milling

*Y. Shadangi<sup>1</sup>, V. Shivam<sup>1</sup>, M. K. Singh<sup>1</sup>, D. Verma<sup>2</sup>, V. Balakrishnan<sup>2</sup>, J. Basu<sup>1</sup>, K. Chattopadhyay<sup>1</sup>, N. K. Mukhopadhyay<sup>1</sup>*

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<sup>2</sup> Indian Institute of Technology Mandi

The influence of mechanical milling (MM), primarily on microstructure, phase composition and hardness, of Al<sub>62.5</sub>Cu<sub>25</sub>Fe<sub>12.5</sub> (at%) quasicrystalline (QC) matrix reinforced with Sn (10, 20 and 30 vol %) has been investigated by the means of X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), differential scanning calorimetry (DSC) and nanoindentation methods. The powder of QC and Sn was milled in high-energy planetary ball mill at 200 r.p.m for 10, 20, 30 and 40 h using WC milling media with toluene as process control reagent. The XRD results indicate that, with increase in the milling duration, the peaks of the QC and Sn becomes broader, leading to the formation of nanostructured composite (NC). It was observed that with increase in the milling duration the QC co-existed with crystalline phases i.e.  $\omega$  [Al<sub>7</sub>Cu<sub>2</sub>Fe and P4/mnc, a = 0.6336 nm and c = 1.481 nm] and  $\beta$  [Al (Cu, Fe) and Pm3m, a = 0.2029 nm]. The crystallite size was found to be ~ 35, 50 and 53 nm for QC reinforced with 10, 20 and 30 volume fractions of Sn respectively, suggesting that the grain refinement decreases with increasing the volume fraction of Sn. This change in crystallite size may be attributed to change in mechanism of MM. In SEM analysis, it was found that the both QC and Sn particles are refined during MM. The Sn particles (rod like morphology) were homogeneously dispersed in the QC matrix as evidenced through SEM – EDS mapping. TEM results confirm the formation of nanoquasicrystalline matrix reinforced with deformed ultrafine-grained Sn particles after MM. The STEM-EDS results show homogenous distribution of elements (Al, Cu, Fe). The Sn particles were immiscible in QC matrix as suggested by XRD and TEM results. Further, the nanohardness was found to be varying as the function of milling duration and volume fraction of Sn particles in QC matrix. The nanohardness of the QC composite was found to be 6.6, 5.2 and 3.8 GPa for 10, 20 and 30 volume fraction of Sn reinforcement respectively. The sequential drop in nanoindentation hardness with the increase in the Sn reinforcement volume fraction may be attributed to the presence of softer Sn phase in the matrix. Therefore, Sn particle may be used as a reinforcement in QC matrix to get a product with optimal hardness, high wear resistance and enhanced fracture toughness.

**ID-106****Nanosized tantalum powder reduced by magnesium gas from tantalum oxide***D-W Lee**Korea Institute of Materials Science*

The pure tantalum metal powder was successfully produced by magnesiothermic reduction of tantalum pentoxide ( $Ta_2O_5$ ).  $Ta_2O_5$  powder with near 200nm in mean particle size reacted with magnesium gas in argon atmosphere at 1,173K for 20 hours. By the reaction, tantalum oxide was transformed to Ta-core and MgO-shell structured particles, which had nearly same size, because the reaction temperature was considerably lower than 3,290K of its melting temperature. The shell component of MgO was fully dissolved in 10% HCl solution for 2 hours at room temperature and the pure tantalum powder was obtained by filtering technique. The phase evaluation, microstructure, crystal size and oxygen content in produced tantalum powders were studied, respectively.

## ID-230

**Fabrication of porous titania (TiO<sub>2</sub>) thin films with a high specific surface area using nano-cellulose and analysis of their characteristics**

*Y. Yoon<sup>1</sup>, G. Yang<sup>1</sup>, H. Noh<sup>1</sup>, S. Kim<sup>1</sup>, W. Lee<sup>1</sup>, S. Lee<sup>2</sup>*

<sup>1</sup> *Sejong University*

<sup>2</sup> *National Institute of Forest Science*

A titania (titanium dioxide, TiO<sub>2</sub>) functioned as a photocatalyst is self-purification substance through an oxidation-reduction process induced by solar energy. To maximize the photo-activity, many re- searches on the mesoporous titania that possesses a high specific surface area have been actively conducted. In this study, we adopted cellulose nanocrystal (CNC) natural substance as a porous template which is easy to be extracted, eco-friendly, and rich in nature to produce the porous titania thin films without removing the template compared to the conventional method. We varied the mass ratio of CNC and titania precursor of titanium(IV) ethoxide (TEOT). After spin-coating the CNC-titania precursor solution on the ITO glass substrate, calcination at high temperature follows to combust the CNC, enabling the formation of porous structure.

By controlling the proportion of CNC contained in the precursor, the porosity, pore volume, and specific surface area of titania thin film can be controlled. Furthermore, calcination temperature was subdivided to check the surface morphology and BET parameters at the various condition. To extend the absorption wavelength from ultraviolet to visible ray region, transition metals such as Co, Mo, Nb, and W were doped into porous titania thin films as an additional process.

FE-SEM, BET, XRD, and XPS were utilized to analyze the morphology, structure and qualitative properties of porous titania thin films. UV-Vis spectroscopy and spectrophotometer were also used to analyze the optical properties and photo-activity. The porous structure of titania films with acicular mesopores consisted of TiO<sub>2</sub> crystallites in the range of 100~200 nm. The porous nature duplicates the original pattern of CNC. The specific surface area of film was 221.6 m<sup>2</sup>/g when the TiO<sub>2</sub>/CNC mass ratio was 0.5 and the calcination temperature was 350. Titania films doped with transition metal that has higher valence electron such as Nb<sup>5+</sup>, Mo<sup>5+</sup>, W<sup>6+</sup> showed improved photocatalytic characteristics and photodegradation efficiency. Furthermore, the surface area of porous titania films was at least 20% higher with doping the transition metal.

Tuesday 3 July afternoon - 15:30/17:00

Parallel Session 2  
**METALLIC GLASSES V**  
Chair: J.M. Pelletier

ID-258

**Evaluation of governing factors for mechanical properties in Ni- Transition metal binary metallic glasses***H. Ahn<sup>1</sup>, H. Oh<sup>1</sup>, C. Ryu<sup>1</sup>, E. Park<sup>2</sup>**<sup>1</sup> Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University,**<sup>2</sup> Seoul National University*

Metallic glasses exhibit excellent mechanical properties, such as high strength, large elastic strain limit and low elastic modulus. Especially, Ni-based metallic glasses are attractive candidates for structural applications since they exhibit outstanding thermal and mechanical properties. However, there is no clear understanding on the factors that influence mechanical properties. To solve this problem, first we carefully check the glass former of Ni-Transition metal (TM=Zr, Ti, Nb, and Ta) binary alloys based on the new glass forming ability (GFA) descriptor considering the thermodynamics of competing crystalline phases without experimental method. Interestingly, Ni<sub>60</sub>TM<sub>40</sub> binary alloys (TM=Zr, Ti, Nb, and Ta) can form a metallic glass ribbon regardless of the kind of TMs, but thermal and mechanical properties diverge greatly according to TMs. To understand the correlation between structure and mechanical properties, we investigate characteristics of atomic bond using high-energy X-ray data and mechanical responses through nanoindentation test. In particular, we statistically analyzed the distribution of shear avalanches, thereby characterizing amorphous structures in the aspect of topological fluctuations of local part. These results could provide effective guidelines for manipulating mechanical properties via metallic glass design through tailor-made atomic structure control.

## ID-73

**Thermoplastic formability of biocompatible Ti- and Zr-based bulk metallic glasses**

*M. Calin*<sup>1</sup>, *S. Bera*<sup>1</sup>, *P. Ramasamy*<sup>2</sup>, *B. Sarac*<sup>2</sup>, *J. Eckert*<sup>2</sup>

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<sup>2</sup>Erich Schmid Institute of Materials Science, Austrian Academy of Sciences (ÖAW)

Bulk metallic glasses (BMGs) exhibit a unique temperature-dependent mechanical behavior, which enables polymer-like processability at temperatures higher than the critical BMG-specific glass transition temperature [1]. Thermoplastic forming of BMGs is uniquely suited to generate micro- and nano-scale surface topographies leading to a stronger cell-material interaction necessary for an optimal osseointegration.

Ti- and Zr-based BMGs are attracting increasing interest as potential biomaterials due to their unique combination of properties: high fracture strengths, large elastic limit, excellent wear and corrosion performances and good biocompatibility [2].

In this work, the thermoplastic forming (TPF) ability for micro-scale surface patterning of two Ni-free Ti- and Zr-based BMGs ( $Ti_{40}Zr_{10}Cu_{34}Pd_{14}Ga_2$  and  $Zr_{48}Cu_{36}Al_8Ag_8$ ) was studied [3]. The alloys were obtained in bulk form by copper mold casting. The surface patterning of the BMGs is achieved by thermoplastic forming into anisotropically etched cavities of silicon chips. Parameters such as temperature and time for optimized pressing conditions while retaining the fully glassy state are determined by thermo-physical and thermo-mechanical measurements. The correlation between the filling depths of the investigated Zr- and Ti-BMG alloys is best described by the formability criterion, which is defined by the ratio of the width of the supercooled to the undercooled liquid region. The highest material flow occurs when the temperatures for the Zr- and Ti-BMGs are selected as 748 K and 693 K, respectively, while retaining a pressure of 40 kN and a time of ~3 min constant. An order of magnitude difference between the viscosities of these alloys and the variation of the maximum applied load during TPF are reflected in the final feature height and geometry. The practicality of the TPF process with high-resolution surface patterning capability, together with their intrinsic properties make the studied BMGs potential candidates for implant applications.

Financial support through the EC (FP7 VitriMetTech-ITN) and ERC-Advanced Grant 'INTELHIB' is gratefully acknowledged.

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## ID-78

**FeNi-based bulk metallic glasses with large plasticity and excellent soft magnetic properties***B. Shen**Southeast University*

Fe-based bulk metallic glasses (BMGs) have attracted great attention due to their excellent soft magnetic properties and high fracture strength, but few applications have been materialized as structural materials because of their brittleness at room temperature. Here, we successfully synthesized an  $\text{Fe}_{39}\text{Ni}_{39}\text{B}_{14.2}\text{Si}_{2.75}\text{P}_{2.75}\text{Nb}_{2.3}$  BMG which exhibits large plastic strain of 7.8 %, high fracture strength of 3.35 GPa and excellent soft magnetic properties, i.e., rather high saturation flux density of 0.88 T, low coercive force of 0.7 A/m and high permeability of 20800. The results indicate that the mutual repulsion between ductility and strength could be renovated in the Fe-based BMGs by the rearrangement of atomic configurations through Ni addition. With proper combination of non- directional metal-metal bonds and directional metal-metalloid bonds, the mechanical properties of FeNi-based BMGs can be improved. Our studies provide a guideline in designing ductile FeNi-based BMGs with high strength, large GFA and excellent soft magnetic properties.



## ID-88

**Role of Yttrium addition on the improvement of the plasticity in the Cu-Zr-Ti system**

*O. Baulin<sup>1</sup>, D. Fabrègue<sup>1</sup>, S. Gravier<sup>2</sup>, S. Cazottes<sup>1</sup>, M. Bugnet<sup>1</sup>, B. Ter-Ovanesian<sup>1</sup>, J-M Pelletier<sup>1</sup>*

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Yttrium is known to exhibit a high atomic radius, contributing to the maximum disorder principle. It also shows a strong affinity with oxygen. This reaction contributes to stabilize the liquid phase and delay the crystallization. Moreover increasing the GFA, micro-alloying of Y is also responsible of an improvement of a lot of properties, as for example, corrosion resistance, thermal stability, biocompatibility and also the plasticity of the sample. However no clear explanations have been presented about this beneficial effect yet. In this work, after determining the optimum quantity of Yttrium to add, the characterization of this material was conducted. 1 at. % of Y in the Cu-Zr-Ti leads to an increase of 2% of plastic strain. The micro-structure was precisely studied using Transmission Electron Microscopy (TEM) observations and some explanation about this improvement can be discussed. Yttrium nano-precipitates with a core-shell structure were observed. This leads to an improvement of the ductility of the material, due to the nano-crystallized areas induced by the precipitates. EDX and EELS analysis were also used to confirm that they correspond to yttria.

Corrosion behavior was also investigated in several electrolyte mediums and 1 at. % Y increases the corrosion potential to -0.23 V/SCE which is close to the Ti-6Al-4V alloy. NaCl solution and NaCl solution with 4g/L of albumin were used. These proteins adsorbed on the sample surface to create a passive level and avoid the immediate dissolution due to the main Cu content. They drastically change the material corrosion behaviour.

## ID-131

**Origin of large plasticity and multiscale effects in FeNi-based metallic glass**

*B. Sarac<sup>1</sup>, Y.P. Ivanov<sup>2</sup>, M. Stoica<sup>3</sup>, J. Eckert<sup>4</sup>*

<sup>1</sup> *Erich Schmid Institute of Materials Science*

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<sup>4</sup> *Montanuniversität Leoben*

Fe-based bulk metallic glasses (BMGs) have attracted great attention due to their soft magnetic properties along with high strength at the expense of plasticity [1]. A newly developed  $\text{Fe}_{50}\text{Ni}_{30}\text{P}_{13}\text{C}_7$  based BMG overcome this limitation by showing extensive compressive plasticity [2]. The large plasticity observed in the newly developed monolithic bulk metallic glasses under quasi-static deformation raises a question about the contribution of atomic scale effects. The main goal of this study is to resolve the origin of large plasticity, which is the multi-scale heterogeneities, from an atomic (on the order of 1-1.5 nm in size) and micro-scale (in several microns) point of view using a combination of an aberration-corrected high-resolution transmission electron microscopy (HRTEM) and nanoindentation techniques [3]. Since Fe and Ni atoms have a very small heat of mixing and similar atomic radii, the GFA of this system decreases as the Ni content increases, which gives rise to nanocrystal formation. Remarkable variations in hardness and elastic modulus measured by the nanoindentation tests and preferential thinning confirm the existence of hard and soft phases for this BMG. Furthermore, we performed systematic simulations of the HRTEM images at varying sample thicknesses, and theoretical model for the estimation of the shear transformation zone size. The findings suggest that the main mechanism behind the formation of softer regions are the homogeneously dispersed nanocrystals, which are responsible for the start and stop mechanism of shear transformation zones and hence, play a key role in the enhancement of mechanical properties.

[1] M. Stoica, S. Kumar, S. Roth, et al., *Journal of Alloys and Compounds*, 483, 632 (2009)

[2] W.M. Yang, H.S. Liu, Y.C. Zhao, et al., *Scientific Reports*, 4, 6233 (2014)

[3] B. Sarac, Y. P. Ivanov, A. Chuvilin, et al., *Nature Communications*, DOI: 10.1038/s41467-018- 03744-5 (2018)

**ID-352****Early plasticity in metallic glasses***D. Tönnies, L. Tian, C.A. Volkert**Institute of Materials Physics, University of Göttingen*

Understanding the emergence of shear bands from smaller deformation entities, such as shear transformation zones, has become a topic of intense research in the past years, with the goal of ultimately mediating the brittle behavior the shear bands cause. However, since shear transformations zones as well as shear bands operate at time and length scales that are barely accessible experimentally, systematic studies must often be performed to gain indirect insight. Here, we use small-scale spherical nanoindentation with different strain rates and contact sizes on metallic glasses to instigate and detect pop-ins, which are believed to be a direct indication of early, collective flow events in the amorphous structure. By applying additional external stresses, thermal and mechanical annealing treatments as well as hydrogen loading, we statistically examine the mechanical response during incipient plasticity under different structural conditions. We discuss our results in terms of local flow event cooperativity that results in shear banding.

Tuesday 3 July afternoon - 15:30/17:00

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY III**  
Chair: C. Maccato

## ID-109

**The effect of reactive surface area of Ni-Ba<sub>0.8</sub>Sr<sub>0.2</sub>Ce<sub>0.6</sub>Zr<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> anodes on the performance of proton-conducting solid oxide fuel cell**

K-T Hsu<sup>1</sup>, S-M Song<sup>1</sup>, P-H Tsai<sup>1</sup>, Y-C Liao<sup>2</sup>, J.S. Jang<sup>1,2</sup>, J-C Lin<sup>1</sup>, S- Lee<sup>1</sup>, I-M Hung<sup>3</sup>, C-S Hsi<sup>1</sup>

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<sup>3</sup>Department of Chemical Engineering and Materials Science, Yuan Ze University

To find the optimum composition combination of NiO and Ba<sub>0.8</sub>Sr<sub>0.2</sub>Ce<sub>0.6</sub>Zr<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (BSCZY) for fabricating the anode materials, the Ni-Ba<sub>0.8</sub>Sr<sub>0.2</sub>Ce<sub>0.6</sub>Zr<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> (Ni-BSCZY) samples with different ratios of NiO and BSCZY were prepared as anode materials by solid state reaction process. In parallel, the BSCZY oxides were also synthesized as proton-conducting electrolyte by solid state reaction process. The porous structure of anode substrates not only provide the mechanical strength to the fuel cells and enable the fuel gases to flow to the electrolyte membrane, but also create excess surface area to form more triple-phase boundary (TPB) by adding NiO in the anode sample. In this study, the effect of NiO contents on the microstructures, surface area, electric conductivity of these Ni- BSCZY anode materials (NiO55-BSCZY, NiO60-BSCZY, and NiO65-BSCZY) were systemically investigated by X-ray diffraction (XRD), scanning electron microscopy (SEM), BET surface area, and four probe conductivity analysis. In addition, three different anode-supported cells containing an identical electrolyte and different composition combinations of NiO and Ba<sub>0.8</sub>Sr<sub>0.2</sub>Ce<sub>0.6</sub>Zr<sub>0.2</sub>Y<sub>0.2</sub>O<sub>3-δ</sub> anode materials were fabricated for I-V curve performance testing and electrochemical impedance spectra (EIS) measurement. The results reveal that the reactive surface area of anode connected to the electrolyte plays an important role on the total cell performance. The cell containing NiO60- BSCZY anode material, possesses the highest surface area 6.91 m<sup>2</sup>/g and lowest total resistance of 2.19 Ω cm<sup>2</sup>, performs the highest power density of 169.2 (mW/cm<sup>2</sup>) at 800°C.

## ID-141

**Highly nanostructured doped NiCo<sub>2</sub>O<sub>4</sub> nanowires as performing cathode materials for Li-O<sub>2</sub> cells**

*D. Giacco<sup>1</sup>, S. Brutti<sup>2</sup>, A. G. Marrani<sup>1</sup>*

<sup>1</sup> *Department of Chemistry, La Sapienza, University of Rome*

<sup>2</sup> *Dipartimento di Scienze, Università della Basilicata*

We synthesized by means of a hydrothermal method highly nanostructured undoped and doped NiCo<sub>2</sub>O<sub>4</sub> phase grown on nickel foam. We adopted them as carbon-free positive electrodes for Li-O<sub>2</sub> cells. For the first time, we investigate the effect of the incorporation of transition metal ions as dopants in the spinel lattice of the NiCo<sub>2</sub>O<sub>4</sub> cubic phase on the electro-catalytic activity of this material towards both the ORR and the OER. The nanomaterials were characterized by X-ray diffraction, field emission scanning electron microscopy coupled with energy dispersive spectroscopy, transmission electron microscopy and X-ray photoemission spectroscopy.

In the case of Cr(III) and Zn(II) doping, the diffraction patterns confirm the growth of a cubic NiCo<sub>2</sub>O<sub>4</sub> phase crystallized in an inverse spinel lattice with minor modification of the cell parameter. As regards the nanomorphology, SEM and TEM images suggest both undoped and doped materials are constituted by porous nanowires formed by crystalline regular particles. The EDS maps of chromium and zinc show their homogeneous dispersion on the nanostructures thus confirming their incorporation as dopants into the spinel lattice.

The surface properties have been analyzed by XPS in order to highlight the redox state of the transition metals and their relative amount on the surface. Our results suggest the substitution of Co(III), Co(II) and Ni(III) centers by Cr(III) and Zn(II) ions, possibly affecting local and macroscopic magnetic properties and modifying the absorption thermodynamics/kinetics of O<sub>2</sub> and electrode reactions intermediates.

The performance in Li-O<sub>2</sub> cells of the undoped and doped NiCo<sub>2</sub>O<sub>4</sub> electrodes were tested in galvanostatic cycling using a non-aqueous electrolyte. Both Cr(III) and Zn(II) doping discloses a remarkable enhancement of the discharge capacity and reversibility in long-term test performed in limited capacity mode. Moreover, pseudo-Tafel data derived by galvanostatic titrations highlight the beneficial effect of doping with transition metal ions on the electrode kinetics both for the ORR and the OER.

ID-168

**Methanol oxidation on nanotubular Pt-Ce-O<sub>2</sub> composites***C.F. Martinez Tovar, A. Robledo, J. Garcia**Instituto Politécnico Nacional-Esiquie*

In recent years, much attention has been focused on cerium oxide (CeO<sub>2</sub>)-based materials for electrooxidation of methanol due to the capability of CeO<sub>2</sub> for oxidizing CO to CO<sub>2</sub>, reducing the CO poisoning of conventional Pt/C anodes. In this study, we report the synthesis of novel highly active and CO tolerance nanotubular Pt-Ce-O<sub>2</sub> materials to be used as anodes in methanol fuel cells. The nanotubular Pt-Ce-O<sub>2</sub> materials were prepared through the substitution of carbon by Ce and O atoms in the hexagonal graphene layers of multiwalled carbon nanotubes and subsequent Pt incorporation. The electrochemical performance of Pt-Ce-O<sub>2</sub> materials was evaluated by cyclic voltammetry and CO-stripping in 0.5M H<sub>2</sub>SO<sub>4</sub> + CH<sub>3</sub>OH solution. The methanol oxidation was followed by in situ differential electrochemical mass spectrometry (DEMS). It was found that remaining carbon in Pt-Ce-O<sub>2</sub> materials promoted high activity in methanol oxidation. Carbon containing Pt-Ce-O<sub>2</sub> nanotubular materials exhibited a high mass activity (400 mA/mgPt) towards methanol oxidation, which is 1.5 times that of conventional Pt/C anodes. Carbon remaining Pt-Ce-O<sub>2</sub> materials showed higher conversion of methanol to CO<sub>2</sub> + methyl formate (HCO<sub>2</sub>CH<sub>3</sub>) than conventional Pt/C, suggesting improvement of the CO tolerance property.

ID-250

**Effect of  $\text{AlCl}_3$  additive on Li-N-H hydrogen storage properties***L. Albanesi<sup>1</sup>, S. Garroni<sup>2</sup>, F. Gennari<sup>1</sup>, S. Enzo<sup>3</sup>, P. Nolis<sup>4</sup>, M. Baró<sup>5</sup>*<sup>1</sup> *Centro Atómico Bariloche - Comisión Nacional de Energía Atómica*<sup>2</sup> *University of Burgos*<sup>3</sup> *University of Sassari and INSTM*<sup>4</sup> *Servei de Ressonancia Magnètica Nuclear (SeRMN)*<sup>5</sup> *Departament de Física, Universitat Autònoma de Barcelona*

Combination of light metal amides with hydrides represents one of the most valid approach for generating promising systems for solid-state hydrogen storage with favorable thermodynamic stability and hydrogen storage reversibility. Among them, the  $\text{LiNH}_2$ -LiH system is one of the most attractive lightweight composites for hydrogen storage thanks to their high gravimetric capacity of 6.5 wt%. However, the temperature required for its re-hydrogenation is still too high for any real application as storage material. For these reasons, different efforts have been addressed on incorporating additives to destabilize the Li-N-H system.

Significant improvement of the hydrogen sorption properties of the  $\text{LiNH}_2$ -LiH system, has been achieved, for example, by introducing  $\text{AlCl}_3$  in the initial mixture by ball milling [1-2]. The new substituted amide displays improved hydrogen storage properties with respect to the pristine Li-N-H system. Additionally, the concurrent incorporation of  $\text{AlCl}_3$  and the presence of LiH are effective for mitigating the ammonia release, which is responsible for the loss of the hydrogen storage capacity. In the light of the above-mentioned facts and considering that  $\text{AlCl}_3$  is a well-known Lewis acid and both  $\text{LiNH}_2$  and LiH are Lewis bases, it is plausible to expect a competitive and free-activated reaction for the couple  $\text{LiNH}_2$ - $\text{AlCl}_3$  and  $\text{LiH}$ - $\text{AlCl}_3$  in the ternary system  $\text{LiNH}_2$ -LiH- $\text{AlCl}_3$ . Therefore, understanding of the reactivity involved at the beginning of these reactions results a crucial step for gain relevant information on the mechanism formation of the new Al-based halide amide phases and their precursors.

In this work a detailed study on the structural modification and phase evolution in the hand-milled samples, is reported for the system  $\text{LiNH}_2$ -1.6LiH-x $\text{AlCl}_3$ . The samples have been systematically investigated by X-ray powder diffraction, FTIR and NMR measurements. It is demonstrated that the reaction between  $\text{LiNH}_2$ -LiH and  $\text{AlCl}_3$  takes place at room temperature in the ternary system without ball milling and thermochemical activation. Furthermore, a competitive reaction between  $\text{LiNH}_2$ - $\text{AlCl}_3$  and  $\text{LiH}$ - $\text{AlCl}_3$  is also confirmed. From these reactions,  $\text{LiAlCl}_4$  and  $\text{NH}_4\text{Cl}$  are detected and their formation achieved under unexpected conditions.

[1] L.Fernández Albanesi, P.Arneodo Larochette, F.C.Gennari, Int.J.HydrogenEnergy38 (2013)

[2] L.Fernández Albanesi, S.Garroni, P.Arneodo Larochette, P.Nolis, G.Mulas, S.Enzo, M.D.Baró, F.C.Gennari, Int.J.HydrogenEnergy40 (2015)



## ID-260

**Hydrogen storage and hydrolysis behaviors of core-shell structured Mg based nano-composites synthesized through arc plasma method***J. Zou, X. Zeng, W. Ding**Shanghai Jiao Tong University*

Mg based materials are promising for the onboard or stationary hydrogen storage since they have the advantages of high capacity, environmental friendliness and low cost. However, the high desorption temperature (~573K) of the Mg hydride and sluggish kinetics have greatly limited its potential applications. Hydrolysis of Mg hydride is thus considered as an efficient way to generate hydrogen instead of the thermal decomposition. However, the formation of  $\text{Mg}(\text{OH})_2$  on the surface of Mg hydride particles may potentially stop the hydrolysis. In the present work, core-shell structured Mg based hydrogen storage materials were prepared through arc plasma evaporation and condensation of Mg-Transition metals (TMs) and Mg-Transition metal fluorides [1-4]. A core shell structure was observed for the Mg based nano-composite materials. These nano-composite materials show good hydrogen storage properties. In particular, the hydrolysis properties of core-shell structured Mg based nano-composite materials are found better than the pure Mg powder prepared under same conditions. The results show that core-shell structured Mg hydrides can be promising materials for the onsite hydrogen generation.

## References:

- [1] Mao JF, Zou JX, Lu C, Zeng XQ, Ding WJ. Hydrogen storage and hydrolysis properties of core-shell structured Mg-MFx (M=Ni, V, La, Ce) nano-composites prepared by arc plasma method. *Journal of Power Sources*, 366 (2017)131-142.
- [2] Zou JX, Zeng XQ, Ying YJ, Chen X, Guo H, Zhou S, Ding WJ. Study on the hydrogen storage properties of core-shell structured Mg-RE (RE=Nd, Gd, Er) nano-composites synthesized through arc plasma method. *International Journal of Hydrogen Energy*, 38(2013)2337-2346.
- [3] Long S, Zou JX, Liu YN, Zeng XQ, Ding WJ. Hydrogen storage properties of Mg-Ce oxide nano-composite prepared through arc plasma method. *Journal of Alloys and Compounds*, 2013; 580, s167-s170.
- [4] Zou JX, Long S, Chen X, Zeng XQ, Ding WJ. Preparation and hydrogen sorption properties of a Ni decorated Mg based Mg@Ni nano-composite. *International Journal of Hydrogen Energy*, 40(2015)1820- 1828.

## ID-72

**Ni-Nb-Zr amorphous membranes: a study of crystallization and hydrogen solubility**

*A. Paolone<sup>1</sup>, O. Palumbo<sup>1</sup>, F. Trequattrini<sup>2</sup>, D. Chandra<sup>3</sup>*

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<sup>2</sup> Sapienza University of Rome

<sup>3</sup> University of Nevada

Metallic amorphous membrane have been largely studied for high grade hydrogen purification [1, 2]. In particular, some Ni-Nb-Zr membranes display a hydrogen permeability of the order of  $10^{-9}$ -  $10^{-8}$  mol m<sup>-1</sup>s<sup>-1</sup>Pa<sup>-0.5</sup>, which is well comparable to that of the benchmark Pd-based alloys [2]. One of the main issues about their use is their propensity to crystallize when heated to temperatures close to those (400-450°C) needed for hydrogen purification, a process which increases atomic density and leads to reduction in hydrogen diffusion pathways. In addition, crystalline phases are more brittle than the amorphous one, thus limiting their operating conditions. The addition of other alloying metals in the Ni-Nb-Zr systems, such as Ta, Hf or Co, has been proposed to increase the resistance to embrittlement [2,3] and the hydrogen permeation.

Here we will present our recent results [2-5] on several melt spun Ni-Nb-Zr membranes regarding thermal stability, mechanical properties and hydrogen solubility. Several substitutions of Zr or Nb have been explored firstly by investigating the crystallization process by means of differential scanning calorimetry. Moreover, hydrogen solubility has been measured by means of a volumetric apparatus. Indeed, solubility is strictly linked to permeability, and they can be obtained one from the other mathematically. Moreover, the knowledge of the hydrogenation properties is fundamental, since the formation of hydrides under certain operation conditions can lead to the failure of the membrane because of the increased brittleness. Absorption data also provide indications about the hydrogen occupancy in the membrane during hydrogenation, which is one of the controlling parameters for the hydrogen permeation. Results suggest that at the beginning of the absorption process the deepest energy levels are occupied, while only shallower energy levels are available at higher hydrogen content, with the available interstitial sites forming a continuum of energy levels.

[1] M. D. Dolan et al. J. Membr. Sci., 285, 2006, 30-55.

[2] S. Sarker et al. Appl. Phys. A, 122, 2016 168.

[3] O. Palumbo et al. Membranes, 6, 2016, 48.

[4] O. Palumbo et al. Energies, 8, 2015, 3944-3954.

[5] O. Palumbo et al. Progress in Natural Science: Materials International, 27, 2017, 126.

**Tuesday 3 July afternoon - 15:30/17:00**

Parallel Session 4  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES III**  
Chair: A. Santagata

**ID-158****Further insights into vapour deposited ultra-stable glasses from dielectric spectroscopy**

*C. Rodríguez-Tinoco<sup>1</sup>, M. Rams-Baron<sup>1</sup>, K.L. Ngai<sup>2</sup>, J. Rodríguez-Viejo<sup>3</sup>, M. Paluch<sup>1</sup>*

<sup>1</sup> *University of Silesia in Katowice*

<sup>2</sup> *CNR-IPCF*

<sup>3</sup> *Universitat Autònoma de Barcelona*

Vapour deposition (VD) burst into the field of glasses a decade ago due to the ability to produce glasses with exceptionally high density and low enthalpy levels (ultra-stable glasses) and particular molecular arrangement. VD glasses became an excellent benchmark to study the dynamical behaviour of glasses, analysing the effect of both density and molecular orientation levels that are not attainable by other means. On the other hand, broadband dielectric spectroscopy (BDS) has proven to be an exceptional tool to investigate the dynamics of liquids and glasses. In particular, BDS is fundamental to understand the nature of fast molecular movements taking place before structural relaxation is triggered in glasses or a very powerful technique to investigate the charge transport phenomena in organic systems.

Here, we study the dielectric properties of vapour deposited glasses of different materials. On one hand, we investigate the effect of ultra-stability on the secondary relaxation processes in glasses of several materials. We show the existence of two clearly differentiated groups of secondary relaxations: those becoming slower in the ultra-stable state with respect to the ordinary unaged glass, mimicking the properties of the structural relaxation, and those becoming faster, indicating certain influence of the particular micro-structure. In this sense, ultra-stability is an ideal tool to understand the origin and role of different secondary processes in glasses. On the other hand, we also show the emergence of a new dielectric process in ultra-stable TPD, a prototypical organic hole transport material, which is not exhibited in the ordinary glass. We relate this to a Maxwell-Wagner process originated from a heterogeneous structure and the enhancement of charge transfer between molecules due to the particular molecular arrangement of VD. In summary, VD emerges as a new exciting tool to get further insight into long-standing issues in glass science such as the classification of secondary relaxations or the inherent heterogeneity of glasses.

## ID-51

**TiO<sub>x</sub>N<sub>y</sub> coatings deposited by Radio frequency magnetron sputtering**

*N. Saoula<sup>1</sup>, L. Bait, M. Azibi, S. Sali<sup>2</sup>, N. Madaoui, A. Hammouche*

<sup>1</sup> CDTA

<sup>2</sup> CRTSE

TiO<sub>x</sub>N<sub>y</sub> films were grown onto 316L stainless steel substrate using radio-frequency (rf) magnetron sputtering from a pure titanium target in Ar-O<sub>2</sub>-N<sub>2</sub> gas mixture with various substrate bias voltages. The aim of this work is to investigate the effect of deposition parameter on the structure and properties of the TiO<sub>x</sub>N<sub>y</sub> thin films for biomaterials applications. The deposited films were characterized by OM, SEM, X-rays diffraction, nanoindentation and potentiodynamic polarization. In order to simulate natural biological conditions, physiological serum (pH = 6.3), thermostatically controlled at 37°C, was used as the electrolyte for the study of the electrochemical properties. Comparison between the corrosion resistance of the uncoated and coated samples showed a reduction in corrosion current density for coated samples compared to the uncoated one. The contact angle measurement was carried out on TiON coatings in order to estimate their wettability characteristics.

## ID-324

**Characterization and piezoelectric properties of promising potassium-sodium niobate (KNN) nanopowders through facile wet method.**

*N. Senes*<sup>1</sup>, *A. Iacomini*<sup>1</sup>, *L. Nuvoli*<sup>1</sup>, *C.L. Santiago*<sup>2</sup>, *S. Garroni*<sup>2</sup>, *D. Neus*<sup>3,4</sup>, *L. Pardo*<sup>5</sup>, *S. Enzo*<sup>1</sup>, *G. Mulas*<sup>1</sup>

<sup>1</sup> *University of Sassari, Department of Chemistry and Pharmacy*

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<sup>4</sup> *Barcelona Institute of Science and Technology*

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Piezoelectricity is the property of many materials to generate an electrical charge, if subjected to mechanical forces (direct piezoelectric effect) or, conversely, to display a mechanical deformation when exposed to an electric field, (reverse piezoelectric effect). The most important piezoelectric ceramic materials are based on mixed oxide crystal system well known as  $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$  (PZT). Due to the ever-increasing restrictions connected to the use of toxic lead-based materials, the developing of lead-free piezoceramics has become one of the most urgent tasks [1]. Among these lead-free candidates, in the past 10 years,  $\text{K}_x\text{Na}_{1-x}\text{NbO}_3$  (KNN) has become one of the most investigated lead-free piezoelectric system due its large  $d_{33}$  (~390-490 pC/N) and relatively high Curie temperatures,  $T_C$ , (~217-304°C), coupled with its high chemical inertia and compatibility with human tissue, which made it optimal for medical devices [2].

Among the type of synthesis, two main preparation procedures are emerged for the KNN, which involves the solid-state reaction routes (SSR) and wet chemistry routes such as sol-gel, Pechini method, hydrothermal, etc. If the SSR route has been considered a fast and solvent-free procedure to produce KNN pellets, the exploitation of the wet-chemistry methods allowed to significantly improve the control of the stoichiometry in the final systems [3].

This contribution aims at providing an overview on the most successful procedures for synthesizing high performing KNN-based systems promising for biomedical applications. Particular emphasis will be addressed to the preparation and characterization of the KNN systems via wet chemistry on the microstructural and electrical properties of the lead-free ceramics [4].

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ID-368

**Hafnium carbonitride ceramics produced by different routes***A. Nepapushev<sup>1</sup>, D. Moskovskikh<sup>2</sup>, A. Rogachev<sup>3</sup>, A. Mukasyan<sup>4</sup>*<sup>1</sup> *Center of Functional Nanoceramics, National University of Science and Technology, Russia*<sup>2</sup> *National University of Science and Technology MISIS*<sup>3</sup> *Merzhanov Institute of Structural Macrokinetics and Materials Science, Russian Academy of Sciences, Russia*<sup>4</sup> *Department of Chemical and Biomolecular Engineering, University of Notre Dame, USA*

Currently, one of the most future-oriented materials for the aerospace industry are ultra-high temperature ceramics. This class of materials can work under extreme conditions, withstand high temperatures, mechanical stress, as well as radiation and wear [1]. Particular attention is paid to carbonitrides of transition metals, which in comparison with nitrides and carbides of these same metals have the best chemical and mechanical properties. Synthesis of these materials is not an easy task due to the high melting points of the main components. Promising routes for obtaining such materials are mechanochemical synthesis and self-propagating high-temperature synthesis (SHS) or combustion synthesis (CS) since they do not require high temperatures and allow obtaining materials with the required composition in a relatively short period. In recent publication from ab initio molecular dynamics calculations it was found that among all carbonitrides  $\text{HfC}_x\text{N}_{1-x}$  might have the higher melting points than any other material [2]. In this connection, the aim of this work was to obtain hafnium carbonitride powders by mechano-synthesis and CS methods with further consolidation via a spark plasma sintering (SPS) in order to obtain compact samples.

Synthesis of carbonitride was carried out according to the following schemes: 1) mechanical treatment of hafnium and graphite powders in a nitrogen atmosphere in an “Activator 2S” planetary ball mill (PBM) during 30 min at a 0.4 MPa gas pressure in the jar; 2) preliminary mechanical treatment of hafnium and graphite powders in the PBM for 5 minutes, followed by CS in a laboratory reactor using different nitrogen pressure. The mechanical treatment carried out in 250 ml steel jars with the ball-to-powder ratio 20:1. Synthesized powders were consolidated into bulk ceramics in a Labox 650 Spark Plasma Sintering device with the temperature up to 2200°C.

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[2] Q-J Hong, A. van de Walle, Phys. Rev. B, 020104(R) (2015)

**ID-271****Development of W-based refractory HEA as fusion reactor materials with low activation elements**

*I.H. Kim, H. Oh, E.S. Park*

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Tungsten is a widely used structural material exhibiting excellent physical properties such as high melting point and high resistance against mechanical wear. Due to these properties, tungsten is also often considered as structural materials in fusion power plants for plasma facing components (PFCs). The PFCs are exposed to very high temperature, heat flux, high energy neutron load, and erosion by plasma. Because of tungsten's low activation and physical properties, it is possible to use tungsten under extreme environments such as the fusion reactor. However, there are some drawbacks. For example, tungsten has low fracture toughness at RT, dramatic softening phenomenon and lower thermal conductivity at a high temperature. In particular, ductile-brittle transition temperature increases by binary alloying compared to pure tungsten. It means that orthodox alloying concepts cannot provide an answer to improve ductility of tungsten alloys. Thus, it is required to develop a new tungsten alloy to tailor these mechanical and thermal properties. In the present study, we developed novel tungsten alloys to enhance mechanical and thermal properties by utilizing design concept of high entropy alloys. Low activation elements were used for application in fusion reactors. To homogeneously cast refractory elements with high melting temperature, we use high power arc melting method. Due to resulting higher configurational entropy tungsten based high entropy alloys exhibit improved strength and thermal conductivity in a wide range, from room temperature to high temperature. This study provides guidelines on how to manipulate properties by controlling configurational entropy in W-based high temperature materials.



## ID-53

**Corrosion properties and bio-evaluation of nanostructured titanium alloys processed by HPT**

*A.M. Jorge Junior<sup>1</sup>, D. Perez<sup>1</sup>, F. Hilario<sup>2</sup>, V. Roche<sup>2</sup>, J.C. Leprêtre<sup>2</sup>, C. Bolfarini<sup>1</sup>, W.J. Botta<sup>1</sup>*

<sup>1</sup> *Federal University of São Carlos*

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Titanium and its alloys are especially appropriate for use in biomedical devices such as orthopedic and dental implants because of a combination of numerous unique properties. Ti has a high specific strength and a low elastic modulus, leading to smaller stress shielding than other competing biomaterials, a high corrosion resistance, even in a biological environment, and excellent biocompatibility. Such properties lead Ti surfaces to hold cell growth and differentiation actively. However, even with a relatively low Young's modulus (100-110 GPa), it is still much superior to the ones of bones (5-30 GPa). Thus, the ensuing stress shielding effect may result in bone resorption. The Young's Modulus of the  $\beta$ -Ti phase is smaller and closer to the bone and can be retained with increasing contents of non-toxic  $\beta$  stabilizing elements (Mo, Ta, Nb, etc). With such element addition, many near- and  $\beta$ -alloys have been synthesized, thus minimizing the stress shielding problem. Nevertheless, adjusted bioactivity is one of the primary requirements for implants. Therefore, their surface needs to be modified for increasing bioactivity (bone-bonding ability). In this work, such an improvement was acquired by ultrafine-grained Ti-alloys after processing by severe plastic deformation using high-pressure torsion (HPT), which also improves wear resistance and mechanical properties.  $\text{Ti}_{13}\text{Nb}_{13}\text{Zr}$  and  $\text{Ti}_{35}\text{Nb}_5\text{Ta}_7\text{Zr}$  alloys were used in this study. Samples were heat treated before HPT (750°C/1h and water quenched). The  $\text{Ti}_{13}\text{Nb}_{13}\text{Zr}$  alloy presented a non-equilibrium metastable martensite phase ( $\alpha'$ ) and a retained  $\beta$ , while in the other alloy only  $\beta$  phase was formed. Samples were processed by HPT for 3 turns with loads of 1 and 4.5 GPa. After HPT,  $\text{Ti}_{13}\text{Nb}_{13}\text{Zr}$  samples presented phase transformation induced by deformation with a decrease of  $\beta$  phase with the load, while only  $\beta$  was present in the  $\text{Ti}_{35}\text{Nb}_5\text{Ta}_7\text{Zr}$  alloy. Grain sizes were reduced to a range of ~500 nm to ~120 nm for both alloys, respectively for loads of 1 and 4.5 GPa. On average, elastic moduli were 60 GPa and 45 GPa, respectively for  $\text{Ti}_{13}\text{Nb}_{13}\text{Zr}$  and  $\text{Ti}_{35}\text{Nb}_5\text{Ta}_7\text{Zr}$  alloys. Corrosion tests showed that the corrosion resistance of both alloys after all processing conditions is similar to that for unprocessed samples. However, a heat treatment for stress relieving improved such property. Bioactivity tests were performed in all kinds of samples, showing different growth rates for different processing conditions and alloys.

Tuesday 3 July afternoon - 17:30/18:30

Poster Session 2  
**NANOSTRUCTURED MATERIALS**  
Chair: A. Marrani

ID-31

**Cellulose nanocrystals isolation from discarded agro-industrial residues***A. Macias-Almazán, J. Lois-Correa, M.A. Domínguez-Crespo**Instituto Politécnico Nacional*

Cellulose is a biopolymer that is renewable, biodegradable and is considered the most abundant polymer on earth. Although higher plants are the most important sources for the production of pulp and paper products, cellulose is also extracted from bacteria, algae, fungi and tunicates. Cellulose nanocrystals (CNCs) also called cellulose nanowhiskers have raised both academic and industrial interest due to their high mechanical properties, low density, high surface area and biodegradability. CNCs also are prone to functionalization and self-assembly into interesting structures. CNCs have shown great potential in a wide range of applications from the automotive industry, to packaging materials, tissue engineering and electronics. CNCs are mainly produced using a top-down hydrolytic approach from biomass. Production methods vary significantly, aiming at maximum CNCs yield and quality. The agro-industrial waste is a source of raw material for this kind of studies since they represent a large area of opportunity for obtaining raw material of cellulosic material. This study aims to efficiently isolate nanocrystalline cellulose (NCC) from agro-industrial waste, specifically wood saw-dust and sugar cane bagasse, to give it a scientific and technological application. Laboratory-level processes were used to isolate cellulose from lignocellulosic residues which included the recovery of by-product and solvent in order to reduce the environmental impact. NCC was achieved using an acid hydrolysis in sulfuric acid, varying the hydrolysis conditions up to optimize the processing parameters according to crystallinity, morphology, obtaining source and yielding. The characterization was carried out by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) and dynamic light dispersion (DLS) to elucidate the chemical structure, crystallinity index, and hydrodynamic radius and size dispersion of de nanocellulose, as well as scanning electron microscopy and transmission electron microscopy to determine their morphology. The results showed that it was necessary to adjust the hydrolysis parameters for sulphuric acid concentration, fiber to acid ratio, temperature and reaction time for each source of cellulose. The isolate NCC reported in this study will be further investigated mixing with graphene oxide and reduced graphene oxide for further applications.

ID-36

**Synthesis, characterization and thermodynamic analysis of WZn nanopowder produced by high energy mechanical alloying for catalytic performance of heavy oil recovery***J. Olvera<sup>1</sup>, E. Montes Hernández<sup>1</sup>, J. García Martínez<sup>1</sup>, E. Celis Martínez<sup>1</sup>, L.G. Díaz Barriga Arceo<sup>2</sup>**<sup>1</sup> Ixtapaluca Institute Of Technology and Higher Education**<sup>2</sup> Metalurgical Department, National Polytechnic Institute*

In this work, the microstructural evolution of a novel WZn alloy during mechanical alloying (MA) was studied. The phases and morphology at each stage of milling were studied by X-ray diffraction, scanning electron microscopy, and high-resolution transmission electron microscopy. The experimental results showed that a WZn solid solution was produced from a mixture of W and Zn powders with crystallite size of 18.3 nm after 100 h of milling. A thermodynamic analysis of the W-Zn system was performed using the Miedema model to study the stability of the MA product. The calculations revealed no thermodynamic driving force in the W-Zn binary to form a solid solution phase in all compositions, suggesting that external energy has to be provided to produce the Mo-Zn phase. The performance of the nano-catalysts in the heavy oil before and after the reaction was analyzed by Fourier transform infrared spectroscopy (FT-IR). As the milling time increased, the ratio of the viscosity reduction of the heavy oil increased.

ID-42

**Effect of micro-sized  $\text{Al}_2\text{O}_3$  particles on properties of electrodeposited Ni-Mo nano-coatings***M. Alizadeh, A. Cheshmpish**Shiraz University of Technology*

In this work, Ni-Mo coating was electrodeposited on mild carbon steel in a citrate bath. Then, micro-sized  $\text{Al}_2\text{O}_3$  particles were added to the electrolytic bath and Ni-Mo/ $\text{Al}_2\text{O}_3$  nanocomposite coatings were deposited. The effect of the  $\text{Al}_2\text{O}_3$  particles on the microstructure, microhardness, and corrosion performance of the Ni-Mo coatings was evaluated. To investigate the microstructural changes and surface morphology of the coatings, as well as the particle distribution in the deposits, optical and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy was utilized. The corrosion behavior of the prepared coatings was investigated in a 3.5 wt. % NaCl solution. The results show that the presence of the  $\text{Al}_2\text{O}_3$  particles in the Ni-Mo coatings change microstructure and also increase microhardness and corrosion resistance of them. It was found that there is an optimum  $\text{Al}_2\text{O}_3$  value in the bath which desirable microstructure, microhardness, and corrosion resistance is achieved.

ID-64

**A single nanotwin FCC phases CuNiCoFeCrAl<sub>0.3</sub> high entropy alloy matrix composites with the in-situ formed TiC nanoparticles***S. Yang, J. Pi**Nanjing Institute of Engineering*

A non-equiatomic CuNiCoFeCrAl<sub>0.3</sub> high entropy alloy composites(HEACs) reinforced by the in-situ formed TiC nanoparticles, produced by mechanical alloying (MA) and spark plasma sintering (SPS). Its microstructure consisted of spherical grains with average size 100-150 nm, among which 10-35 nm nanoparticles of TiC were identified. X-ray analysis and transmission electron microscopy studies with micro-analysis confirmed predominant presence of a nanotwined single face-centered cubic solid solution with TiC nanoparticles. The yield stress, fracture strength and plastic strain and Vickers hardness of TiC-reinforced CuNiCoFeCrAl<sub>0.3</sub> HEACs are as high as  $2040 \pm 20$  MPa,  $2150 \pm 15$  MPa and  $21 \pm 0.50\%$  and  $653 \pm 16$  Hv, respectively.

ID-65

**Excess conductivity and pseudogap in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  nanolayers**

L. Omelchenko

B. Verkin *ILTPE of NASU*

After thirty years since the high-temperature superconductors (HTSC's or cuprates) discovery the physics behind the pairing mechanism which allows the Cooper pairs formation at  $T > 100$  K still remains unknown.

We believe the PG to be due to preformed pairs (local pairs) formation [2] but the pairing mechanism is very likely of a magnetic type [1, 3]. Thus, the comprehension of the interplay between superconductivity and magnetism is widely considered to be one of the great challenges of the condensed- matter physics [1-3].

To clarify the issue, we studied the fluctuation conductivity (FLC) and PG in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$  -  $\text{PrBa}_2\text{Cu}_3\text{O}_{7-\delta}$  (YBCO-PrBCO) superlattices (SL's) and YBCO-PrBCO double-layer films (so-called "sandwiches", SD's) with different layer composition, prepared by pulsed laser deposition.  $\text{Pr}^{3+}$  atoms are known to have an intrinsic magnetic moment,  $\mu_{\text{eff}} \approx 3.58\mu\text{B}$  and  $\mu_{\text{eff}} \approx 2\mu\text{B}$  in the PrBCO compound. Simultaneously pronounced maximum of  $\Delta(T)$  appears at high  $T$  and gradually increases along with NPr. The maximum becomes more pronounced for SL3 and SD2. For the first time such  $\Delta(T)$  with descending linear region below  $T_{\text{max}}$  was observed for magnetic  $\text{SmFeAsO}_{0.85}$  between the structural transition temperature  $T_s = 150$  K and  $T_{\text{SDW}} = 130$  K which corresponds to the antiferromagnetic ordering of Fe spins density wave, it is believed to be the most noticeable feature of the magnetic influence in the HTSCs [2]. To confirm the conclusion, we have compared the results obtained for SL3 and SD2 with those found for  $\text{SmFeAsO}_{0.85}$  and  $\text{EuFeAsO}_{0.85}\text{F}_{0.15}$  [3]. Thus, one may conclude that it is very likely in YBCO-PrBCO compounds with enhanced Pr content, as well as in FeAs superconductors, the transition into the SDW state with decrease of temperature seems to be very possible. Thus we can say that the basic mechanism of the interplay between the superconductivity and magnetism could be the same in different kinds of magnetic superconductors.

[1] A.A. Kordyuk, *Low Temp. Phys.* vol.1, №41, 2015, p.319.

[2] A. Solovjov, *Rijeka: InTech*, 2012, p.137.

[3] A.L. Solovjov, L.V. Omelchenko, et al, *Mater. Res. Express*, Vol.3, 2016, p. 076001(1-13).

ID-66

**Easy-plane ferroborates. Magnetopiezoelectric effects***T. Gaydamak, V. Fil**B.Verkin Institute for Low Temperature Physics and Engineering of the National Academy of Sciences of Ukraine*

Rare-earth borates with formula  $RFe_3(BO_3)_4$  ( $R = Y; La-Nd; Sm-Er$ ) are popular object of study because they the materials which combine magnetically ordered and ferroelectric media properties. This is why ferroborates belong to the family of multiferroics [1].

Since ferroborates belong to noncentrosymmetric class 32, the direct piezoelectric effect (PE) is allowed in these crystals. We have investigated the piezoelectric properties of  $SmFe_3(BO_3)_4$  and  $NdFe_3(BO_3)_4$  single crystals using the acoustic method [2]. It was found that in those compounds, the value of the piezoelectric modulus  $e_{11}$  in the paraelectric phase ( $\approx 1.4 \text{ C/m}^2$ ) was almost an order of magnitude higher than that of the  $\alpha$  - quartz, and, therefore, such compounds may be recommended for technical applications.

In addition to the above-mentioned direct PE in multiferroics the indirect PE may exist. It consists in the joint action of the magnetoelastic and magnetoelectric mechanisms. Due to magnetoelasticity deformation changes the state of magnetic variables and through the magnetoelectric coupling excites the electric field (and vice versa). This effect was first discovered in samarium ferroborate [3].

In  $NdFe_3(BO_3)_4$  direct renormalization of the piezoelectric interaction in a magnetically ordered phase is observed [4].

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ID-81

**Size-dependent longitudinal relaxivity of Tb-doped Gd<sub>2</sub>O<sub>3</sub> nanoparticles for potential MRI and optical imaging***T. Atabaev**Nazarbayev University*

In this study, fluorescent Tb-doped Gd<sub>2</sub>O<sub>3</sub> nanoparticles with different sizes have been synthesized for potential magnetic resonance MRI and optical imaging. As the main goal of our study, we investigated the influence of the nanoparticle size on the water proton relaxivity rate. We showed that the high longitudinal relaxivity value was observed for smaller-sized nanoparticles, implying that surface-to-volume ratio is the main factor affecting the longitudinal relaxivity of prepared samples. In addition, room-temperature photoluminescence study revealed that prepared nanoparticles could emit strong fluorescent signals in blue and green regions. The excellent dual-imaging abilities of prepared nanoparticles could be used for potential nanomedical applications.

ID-135

**Plasmochemical synthesis of nanopowders of components of heavy tungsten alloys in thermal plasma flow***A. Fadeev, A. Samokhin, N. Alekseev, M. Sinayskiy, I. Pakhilo-Daryal, Y. Tsvetkov**Institute of Metallurgy and Materials Sciences RAS*

Synthesis of nanopowders of metal systems W (90 mass %)-Ni-Fe and W (80 mass %)-Cu is carried out in thermal plasma flow generated in DC arc plasma torch by rated power of 30 kW. The plasma jet is generated in DC arc generator (plasmatron) with the different characteristics of a plasma jet. The nanopowders of components of heavy tungsten alloys have been produced as nanoparticles by chemical condensation from vapor in thermal plasma jet at atmospheric pressure. As initial raw materials were used mix of tungsten oxide  $WO_3$  with NiO,  $Fe_2O_3$ , CuO and also mix of  $WO_3$  with metal Ni and Fe. The mix of powdery raw materials is injected into the hydrogen containing thermal plasma flow on the basis of argon, nitrogen, and their mixes on an exit from a nozzle plasma generator and provides the subsequent formation of vapor of end products. Formation of nanoparticles occurs under auto quenching of high temperature flow in the reactor with confined plasma jet. The nanopowder formed a layer on the inner surfaces of reactor and also was collected at the bag filter. Due to heat transfer via water-cooled reactor walls the sufficiently low temperature was maintained in the deposited layer, preventing sintering of the nanopowder. Thermodynamic analysis of W-Ni-Fe-O-H and W-Cu-O-H systems at temperatures of 400-5000 K shows that after cooling of the high-temperature system, the condensation of metals (Ni + Fe, Cu) occurs in the presence of tungsten condensed phase. This suggests the possibility of the formation of particles with the core-shell structure. The nanoparticles produced are analyzed by TEM, HRTEM, SEM, ESD, XRD and BET techniques. The powder products consist of nanoparticles with a size in a range of 10-150 nm, specific surface area (SSA) varies in the range 4 – 8 m<sup>2</sup>/g. Nanoparticles have mainly spherical form. The results of HR-TEM show that the obtained nanoparticles have a core-shell structure, when the core is - tungsten, and the shell is Cu or Ni-Fe alloy. Nanosized metal compositions have total oxygen impurity 1.3-1.5 mass. %. Heat treatment at 600 °C in hydrogen atmosphere decrease oxygen content to 0.5 %. The results of experiments show that the one-stage plasma process may be developed for the production composite nanopowders which are components nanostructure heavy W-based alloys.

The work was carried out according to the Russian Federation state task No. 007-00129-18-00 and Program of Basic Research of the Presidium of the Russian Academy of Sciences P-37.

ID-138

**Determination of average grain size and grain size distributions of nanocrystalline materials - a comparative study including t-EBSD, TEM and XRD***J. Schmauch, C. Braun, M. Johannes Deckarm, R. Birringer**Universität des Saarlandes*

Properties of polycrystalline materials generally depend on the grain size  $D$  of the constituting crystallites and the associated share of grain boundaries which scales as  $1/D$ . In particular, the properties of nanocrystalline materials are strongly influenced by the presence and nature of grain- or phase boundaries but also by the character of the grain size distribution. The latter is first and foremost determined by the synthesis route of the material.

In the limit of very small grain sizes ( $D < 100$  nm), i.e. the case of a real nanocrystalline structure, wide-angle X-Ray scattering is a common method to determine the average grain size of the microstructure. However, smaller grain sizes involve i.a. a significant increase in the local variation of lattice strain, which renders a precise determination of grain sizes challenging; especially for materials with high elastic anisotropy. Therefore, we discuss a whole powder pattern modelling (WPPM) approach [1] to explicitly capture the complexity of the problem and extract meaningful grain size information.

An alternative approach to determine the grain size distribution is based on analysing images captured in a TEM (traditional bright and dark field images or automated crystal orientation mapping (ACOM-TEM)). In addition, a few years ago transmission EBSD (t-EBSD) has been established as a new method to quantitatively analyze average grain sizes and grain size distributions which offers – in contrast to conventional EBSD – an improved spatial resolution in the range of a few nanometers.

When comparing average grain sizes measured by different methods care must be taken. The mean grain size evaluated by X-Ray diffraction is a volume average while the data measured by t-EBSD and TEM represent an average over a cross-sectional area, i.e. it is an area averaged value. In contrast to x-ray diffraction, t-EBSD and TEM yields direct evidence of the grain-size distribution and thus offers the possibility to calculate all moments and hence averages of the distribution function. It is important to note that x-ray diffraction and dark field images are sensitive to coherent scattering regions which can be smaller than grain size measured by t-EBSD or TEM due to lattice defects like stacking fault or twin boundaries. All these aspects will be discussed in this contribution exemplarily for an inert-gas condensed PdAu-sample with average grain sizes below 20 nm.

[1] P. Scardi and M. Leoni, Acta Cryst. A57 (2001) 604

ID-162

**Structural and magnetic properties of MnZnO composites synthesized from waste alkaline and Zn/C batteries***M.V. Gallegos<sup>1</sup>, M.A. Peluso<sup>1</sup>, L.C. Damonte<sup>2</sup>, J.E. Sambeth<sup>1</sup>*<sup>1</sup> *CINDECA (Fac. Cs. Exactas UNLP, CCT CONICET LA PLATA), La Plata, Argentina*<sup>2</sup> *Instituto de Física La Plata – (IFLP, CONICET – FCE UNLP), La Plata, Argentina*

Spent alkaline and zinc–carbon batteries were subjected to a biohydrometallurgy process, in order to recover manganese and mixed manganese zinc oxides. The obtained products were used as starting materials for several new compositional systems containing manganese which crystallized in the spinel structure being their structural and magnetic properties also studied.

Two solids were synthesized, one of them prepared by chemical precipitation with NaOH (ZnMnR) and  $\text{KMnO}_4$  (OMR). The solids were filtered, washed with distilled water, dried at 120 °C and calcined in air at 500 °C during 2 h. Mn and Zn content were determined by atomic absorption spectrophotometry (AAS) using a Varian AA 240 spectrophotometer. Quantitative analysis of the composition of the samples were carried out with a scanning electron microscope provided with energy dispersive X-ray analysis (SEM-EDS) using a Philips SEM 505 microscope. Prepared materials have been extensively characterized using transmission electron microscopy (TEM, JEOL JEM-100CXII), X-ray diffraction (XRD) and FTIR spectroscopy. Optical characterizations were carried out by measuring the diffuse reflectance spectroscopy. All spectra were taken in the range of 200–800 nm using a Perkin Elmer Lambda 35 UV-vis spectrophotometer with integrating sphere attachment. The magnetic properties of the samples were measured by a Quantum Design MPMS-5S superconducting quantum interference device (SQUID) magnetometer at different temperatures. The effect of Mn content on the optical and magnetic properties was analyzed in order to evaluate the use of the recovered materials for different technological applications.

ID-177

**Kinetics study on oxidation of nano- and micron-sized diamond by using a master kinetics curve model***W. Chen, M. Teng**National Taiwan University*

Diamond is an important material with many applications due to its unique characteristics, such as excellent thermal conductivity, highest degree of hardness, low friction and electrical non-conductivity. Although the understanding of the oxidation behavior of diamond is crucial in both industry and basic science, the mechanism of diamond oxidation is still uncertain. In this study, we investigate the relationship between the particle size and oxidation rate of diamond, as well as the possible mechanism of the reaction. A series of diamond powders with different sizes (from 50 nm to 100  $\mu\text{m}$ ) were oxidized by using a thermal gravimetry analyzer (TGA) under various isothermal conditions. The data were then analyzed by a Master Kinetics Curve Model (MKC), which was derived from a general reaction rate equation by us earlier. The oxidation trends of nano- and micron-diamond are similar in the early and middle stages, but with some differences in the final stage. All the samples oxidized at a rate proportional to their specific surface areas in the early stage, but accelerated in the middle and final stages. Preliminary results showed that the MKC model can be used to analyze and predict the oxidizing behaviors of diamond. The apparent activation energies of the oxidation of 50 nm, 100 nm, 10  $\mu\text{m}$ , 50  $\mu\text{m}$  and 100  $\mu\text{m}$  diamond powders were 205.8 kJ/mol, 273.5 kJ/mol, 312.6 kJ/mol, 176.3 kJ/mol, and 138.4 kJ/mol, respectively. The MKC model is a possible universal model; it has been proved useful in the analysis of various reactions, including thermal decomposition, phase transformation, simple chemical reactions, and sintering. However, the MKC model still has some limitations; for example, the MKC model can only analyze reactions with one dominant mechanism. From the results of this study, it is clear that diamond oxidation is controlled by one dominant mechanism.

ID-195

**Production and characterization of magnetic nanoparticles**

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<sup>5</sup> *INFN Sez.di Napoli*

Nanoparticles are found to be useful in many research fields. In particular SmCo magnetic nanoparticles can be used in medicine, pharmacology, electronics, and environmental studies. We obtain SmCo nanoparticles by using a laser ablation technique. Results of this laser ablation technique for NPS production are reported like SEM, TEM images and X-Ray measurements. These analyses allow to control the nanoparticle size, and to discuss their magnetic properties.

ID-196

**Synthesis of crystalline nanocomposites of zinc sulfide (ZnS, ZnS/ZnO) with potential photocatalytic activity for hydrogen production***L.E. Puentes Prado, M.R. González Galindo, C. Gómez Solís**Universidad de Guanajuato*

A fundamental investigation of the interface properties of coupled semiconductor photocatalysts in view of enhancing visible light activity is presented. As typical semiconducting heterostructures of ZnS, the crystalline zinc sulfide (ZnS) thin films were prepared by chemical bath deposition (CBD). Followed by deposition of zinc oxide (ZnO) nanofilm using spin coating. Electrochemical Impedance Spectroscopy (EIS) and Analysis of Chronoamperometry (CA) elucidate the electrochemical behavior of thin films, the structural and morphological characteristics of films have been investigated by Ultraviolet-visible spectroscopy (UV/vis), Atomic-force microscopy (AFM), Scanning Electron Microscopy (SEM) and X-ray Photoelectron Spectroscopy (XPS). We show by photoemission spectroscopy that modification of ZnS with submonolayer films of ZnO, two materials with band gaps larger than 3.6 eV, results in an effective surface band gap narrowing to 3.29 eV. This reduces the photoexcitation threshold energy and thus potentially enhances the solar energy conversion capabilities of such a heterostructure photocatalysts. The Monitoring by Gas Chromatography (GC) of ZnS-ZnO films heterostructures also exhibited a higher photocatalytic performance for H<sub>2</sub> evolution from water splitting under visible light irradiation at 25°C. This study offers a novel way of fabricating semiconductor composites for high-efficiency photocatalysis applications.

ID-217

**Variation of growth rate of metal oxide on deformed copper surfaces***H. Lee, H. Shin*

KITECH

It was investigated that the growth rate of cuprous oxide,  $\text{Cu}_2\text{O}$ , was varied with oriented copper surfaces. The cuprous oxide has been well known as that the band gap energy is ranging 2.0~2.3 eV with red to dark-red color. Although more oxide layers on the metal surface do not help to achieve the mechanical properties, it is better to exhibit the aesthetic colors or shapes. In particular, the mixed colors from cuprous oxide and copper surface can be perceived emotionally by human eyes and being recently applied into the exterior materials of premium refrigerator, smart IOT electronics and so on. However, the effect of the structure of cuprous oxide and the color changes has not been studied. We extended the scheme of research on color of casted copper to the textured surfaces of copper by rolling process. The growth of cuprous oxide on the rolled copper was accelerated by heating from RT to 600 °C, and the kinetic data on growth rates was shown with parabolic model based on diffusion mechanism and logarithmic inversed model based on synthesis mechanism, respectively. The color of metal was analyzed by spectroscopy and the reflectance of L, a, b\* was obtained and visualized on the chromaticity diagram.



ID-226

**Excitation of coherent vibrations of nanoparticles of different shapes***F. Toschi, D. Catone, P. O'Keeffe, A. Paladini**CNR-ISM, Division of Ultrafast Processes in Materials (FLASHit)*

Changing the shape of a nanoparticle (NP) is a very powerful means of finely tuning the plasmonic properties of the system. The particle shape has a dramatic effect on the position of the plasmonic resonance and also additional resonance modes appear due to a reduction of the symmetry of a particle. For example, the peaks of the UV-Vis extinction spectra of Ag nanotriangles (NTs) have been assigned as an in-plane dipole peak, an in-plane quadrupole (or higher order: octapole, decapole, etc.) peak, and out-of-plane dipole and quadrupole resonances [1].

Time-resolved pump and probe spectra of NPs with different shape show a spectral modulation as a signature of a mechanical vibration induced by the pump pulse, as described by Hartland [2] and L. Bonacina et al. [3] in their works on Gold Nanorods and Silver Nanotriangles, respectively. Symmetric vibrations of the particles are responsible for this modulation and affect the plasmon peak of the NP.

In this work we investigate the coupling between these coherent vibrations and the local surface plasmon resonances of different kinds (Silver and/or Gold) of lower symmetry (relative to spheres) NPs, as nanotriangles, nanorods, core-shell NPs, multi-face NPs (hexagonal, octagonal, etc.).

The dynamics of the plasmon resonances of these materials are probed through femtosecond transient absorption spectroscopy (FTAS). The NPs dispersions are excited with a pump pulse and the extinction is monitored by a white light probe (400-800 nm).

The results confirm that the coherent vibrations are strictly correlated with the shape on the NPs under investigation and show how the vibrations and plasmon resonance of the NPs interact as shown in the FTAS spectrum.

The shift and/or broadening of the plasmon peak can be ascribed to the geometry alteration due to the mechanical vibration of the NPs induced by the vibrations of the NPs.

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ID-255

**Synthesis and characterization of zinc oxide for UV-Radiation absorption***S. Valencia Rodríguez, M.R. Galindo González, R. Fuentes Ramírez**Universidad de Guanajuato*

Zinc oxide is a photoactive material by excellence on a nanometer scale its properties are enhanced. In this study, chemical and physical properties of nanosized zinc oxide were studied. Nanoparticles were synthesized by sol-gel method in order to get a small particle size, low cost synthesis process without use of surfactants and easy scalable process. Also, zinc oxide was doped with chitosan for the purpose of study the biopolymer influence on its semiconductor properties. Electro-chemical properties were studied by Galvano Electrochemical Impedance Spectroscopy (GEIS) and chronoamperometry (CA). Zinc oxide was characterized by UV Spectroscopy, X-Ray Diffraction, Diffuse Reflectance and Raman Spectroscopy, Scanning Electron Microscopy (SEM). The surface morphology of treated leathers was observed using Scanning Electron Microscopy (SEM) and the elemental analysis was performed by Energy Dispersive Spectrometer (EDS). It was tested different solvents compatibles with finish coating leather in order to obtain the most stable colloid possible. GEIS results evidenced the electric resistance behavior to different concentrations. Through X-Ray Diffraction analysis found the average crystal size of synthesized nanoparticles was 9.63 nm. To lower concentrations electrical resistance was increased and addition of chitosan to nanomaterial increased it to. Band gap calculated was 3.48 eV which approaches to [1], value reported in the bibliography. It was found zinc oxide absorb UV radiations between 350–400 nm which it's characteristic for this material.

ID-261

**A study of the atomic segregation on the surface of bimetallic nanoparticles Pd-Pt***C. Rodríguez-Proenza<sup>1</sup>, A. F. García-Ruiz<sup>2</sup>, R. Pérez<sup>3</sup>, R. Esparza<sup>3</sup>**<sup>1</sup> Posgrado en Ciencia e Ingeniería de Materiales, Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México**<sup>2</sup> UPIICSA-COFAA, Instituto Politécnico Nacional. On sabbatical year at CFATA-UNAM.**<sup>3</sup> Centro de Física Aplicada y Tecnología Avanzada, Universidad Nacional Autónoma de México*

Bimetallic nanoparticles are of interest since they lead to many interesting electrical, chemical, catalytic, and optical properties. They are particularly important in the field of catalysis since they show superior catalytic properties than their monometallic counterparts. The structure of bimetallic nanoparticles depends mainly on the synthesis conditions and the miscibility of the two components. In this work, PdPt bimetallic nanoparticles were synthesized through the polyol method, and characterized using spherical aberration (Cs) corrected scanning transmission electron microscopy (STEM). High-angle annular dark-field (HAADF)-STEM images of the bimetallic nanoparticles was obtained. The contrast of the images shows that the nanoparticles have alloy structure with an average size of 8 nm. Beside with the characterization of the nanoparticles, a systematic study on structural evolution and atomic surface segregation of a 923-atoms PdPt bimetallic nanoparticle with an alloyed structure by using classical molecular dynamics simulations has been performed.

In this presentation, some results of these studies will be shown by means of images of the synthesized nanoparticles observed directly and characterized in the electron microscope as well as several stages of the simulations where it is possible to appreciate the atomic distribution on the surface of the Pd-Pt bimetallic nanoparticles.

ID-270

## Photocatalytic Titania/Silver nanomaterials for the recognition and degradation of pollutants

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Nanostructured materials exhibit peculiar chemical and optical properties, which find applications in heterogeneous catalysis and pollutant degradation. Titania in the anatase form is currently used in the photocatalysis of many reactions involving pollutants, by UV irradiation. The catalytic activity of titania can be enhanced by doping with metal nanoparticles [1-3] and the identification of the reaction products can be performed by Raman scattering. In this regard, the low sensitivity of the Raman measurements can be overcome thanks to the huge intensification of the spectral signal of reagents and products adsorbed on silver or gold nanoparticles by means of the SERS (surface-enhanced Raman scattering) effect. Here Ag/titania nanoparticles have been obtained by a one-pot procedure, by laser ablation of a titanium target in aqueous AgNO<sub>3</sub> solution. In this way, titanium is oxidized to TiO<sub>2</sub>, whereas silver ions are reduced to metal by galvanic replacement. This procedure allowed obtaining titania colloidal nanoparticles coated with silver, as revealed by TEM and UV-vis measurements. Aromatic nitroderivatives are pollutants of particular attention, because of their toxicity and mutagenicity. Here, 2-amino,5-nitropyridine (ANP) is chosen to check the degradation efficiency of our Ag/titania nanocomposites. When ANP is adsorbed by addition to the colloidal dispersion, a SERS spectrum is obtained corresponding to that usually observed in silver colloids. However, sizeable spectral changes occur after prolonged irradiation. In particular, the SERS bands assigned to bending and stretching modes of the nitrogroup decrease in intensity, whereas a band around 1515 cm<sup>-1</sup> becomes stronger. This evidence, which is not observed in pure Ag colloids, can be attributed to degradation of ANP with formation of 2,5-diaminopyridine. The photocatalytic efficiency has been evidenced by SERS spectra under visible irradiation, instead of UV irradiation, as generally occurs with non-doped titania. This study paves the way to the use of these nanomaterials for the trace identification of environmental contaminants and their photodegradation.

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ID-275

**Study on improved cements with Graphene Oxide***R. Mancini<sup>1</sup>, D. Mirabile Gattia<sup>1</sup>, F. Girardi<sup>2</sup>, L. Petrucci<sup>1</sup>*<sup>1</sup> ENEA - SSPT-PROMAS-MATPRO<sup>2</sup> ENEA - FSN-FISS-CRGR

The preparation of reinforced cements is an important field of research and different approaches are followed, as for example modifying the composition, in order to obtain composites with improved properties. In this work the preparation of Portland Cement with Graphene Oxide is reported. Graphene oxide is a 2D nanometric material which showed interesting properties and it could be used for different applications: composite materials, energy storage and conversion, catalysis, sensors, field emission devices and nano-scale electronic components.

In this work Graphene Oxide (GO) has been produced by using modified Hummers method [1]. After the synthesis the material has been purified, by filtration in porous media, and washed in order to remove any acid traces. Graphene oxide has been mixed with cement in different ways in order to ascertain the suitable method to obtain optimized results. In one case it has been mixed by adding a suspension of GO in water and in the second case by mixing directly the powders before adding water.

Samples with different concentrations of GO (0.03%, 0.039%, 0.05%, 0.06%) have been prepared: GO, water and cement were mixed and stirred to obtain GO-cement paste. Cubic samples with 1 cm side were left to set in an environmental test chamber with controlled humidity and temperature in order to obtain reproducible results and complete curing of the paste according to the UNI EN 206-1: 2006. After 28 days the samples have been investigated by different techniques: Thermogravimetric Analysis (TGA), Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD) and mechanical tests. SEM allowed to study the microstructure and identify the GO inside the cement matrix. SEM images revealed, even at low concentrations, how GO is strongly interconnected with the matrix and homogeneously dispersed within it. The GO is present in the form of large sheets, even if some sub- and micrometric aggregates were observed. The sheets seem to “contain” the matrix particles as a sort of tie-sheet and partially filling the porosities. The compressive trials were performed by an uniaxial press averaging results from three tests per type of sample. The samples showed a typical hour-glass shape after breakage. Surprisingly low quantities of GO added to the cement demonstrated to increase significantly the mechanical performances of the base cement. This work reports results which are promising for the development of new cements for particular applications.

ID-278

**Synthesis and characterization of Ta-Nb-V-Ti-W high entropy alloy by mechanical alloying and spark plasma sintering***D.H. Song, J.S. Park, J.K. Lee**Kongju National University*

Most conventional alloys have been based on a single principal element with several minor elements being added to modify their microstructure and properties. High-entropy alloys (HEAs) are defined a class of multicomponent alloys consisting of five or more principal elements with equal or near equal compositions. HEAs form stable solid-solution phase with simple fcc or bcc structures by the high mixing entropy. Recently the study of HEAs has attracted among the scientists' interest due to properties such as high temperature strength, high corrosion, promising resistance to wear oxidation. In this study, we report the synthesis and characterization of the Ta<sub>20</sub>Nb<sub>20</sub>V<sub>20</sub>Ti<sub>20</sub>W<sub>20</sub> HEA alloy by mechanical alloying (MA) and spark plasma sintering (SPS). The HEAs synthesized by high energy ball milling followed by spark plasma sintering. Structural characterization was performed using X-ray diffractometry (XRD) and scanning electron microscopy (SEM) with energy dispersive spectrometer (EDS). Compressive properties were measured at room temperature with a strain rate of  $1 \times 10^{-4} \text{ s}^{-1}$ .

ID-309

**Effect of Mn in ZnO using DFT Calculations: Magnetic and electronic changes***M.V. Gallegos<sup>1</sup>, C.R. Luna<sup>2</sup>, L. C. Damonte<sup>3</sup>, J.E. Sambeth<sup>1</sup>, P.V. Jasen<sup>2</sup>*<sup>1</sup> CINDECA (Fac. Cs. Exactas UNLP, CCT CONICET LA PLATA) La Plata, Argentina<sup>2</sup> Instituto de Física del Sur (IFISUR, UNS-CONICET) y Departamento de Física, Universidad Nacional del Sur, Bahía Blanca, Argentina<sup>3</sup> Instituto de Física La Plata – (IFLP, CONICET – FCE UNLP), La Plata, Argentina

The zinc oxide (ZnO) is classified as a transparent semiconductor, with a wide band gap of 3.4 eV and a large exciton binding energy of 60 eV. The ZnO material which crystallizes in the wurtzite structure is piezoelectric material. This material can be obtained with a variety of techniques such as vapor phase transport, chemical vapor deposition and sputtering. Each technique used involve different growth mechanisms resulting in bulk crystals with defects or/and impurity background, which affect the electrical and optical properties of bulk. Native or intrinsic point defects -such as vacancies, interstitials and antisites- have long been believed to play a central and even more important role in ZnO. In the other hand, p-type doping of ZnO has attracted considerable attention due to its potential in several areas as optoelectronic devices. Particularly, Mn-doped ZnO has attracted interest in the last years since Mn is incorporated substitutionally at the Zn site. The present work studies the properties of Mn-doped ZnO, and the effect in some chemical and physical properties when charged oxygen vacancy (VOq) are present in the bulk system. First-principles calculations based on Density Functional Theory (DFT), implemented in the Vienna Ab initio Simulation Package (VASP) code is used. Moreover, for improve the results for Zn and Mn species the Hubbard model is taken account.

The results shown that the ZnO bulk has non-magnetic behavior; but the substitution of one Zn for one Mn atom leads to an increase of magnetic moment from 0.00  $\mu_B$  to 4.39  $\mu_B$  per atom. This value is close to the value of 5.0  $\mu_B$  predicted for purely ionic  $Mn^{2+}$  with five unpaired 3d electrons, corresponding to a ferromagnetic state. Regarding to the semiconductor behaviour, the obtained results exhibit that the semiconductor nature still remains with Mn incorporation, leading to a band gap ( $E_g$ ) reduction of 70 % respect to ZnO bulk, from 1.76 eV to 0.64 eV. The reduction in  $E_g$  arises from the new states that are induced in the forbidden zone due to the Mn d-electrons. These facts do the system Mn-doped ZnO a promising candidate for designing the first ferromagnetic piezoelectric material.

ID-323

**Shape change of submicron nickel powder under hydrogen and nickel chloride vapor***S. Yang<sup>1</sup>, D.S. Kim<sup>2</sup>, N.Mo. Hwang<sup>2</sup>*<sup>1</sup> Korea Institute of Industrial Technology (KITECH)<sup>2</sup> Department of Materials Science and Engineering, Seoul National University, Korea

The shape of the Ni particles is important. A spherical shape is favored for an electrode material in multilayer ceramic capacitor (MLCC) due to high packing density. A cubic shape is favored for applications in catalysts and bioseparation due to its higher magnetic property than a spherical shape. It was found that cubic Ni particles which has a facecentered cubic (fcc) crystal structure, can be synthesized by chemical vapor deposition (CVD). In this study, to examine whether the cubic shape of Ni particles synthesized by CVD is the growth or the equilibrium shape, the shape changes of Ni particles by annealing under H<sub>2</sub> and NiCl<sub>2</sub> atmospheres were observed. It was confirmed that H<sub>2</sub> and NiCl<sub>2</sub> vapor favor respectively spherical and cubic shapes, which indicates that NiCl<sub>2</sub> stabilizes the {100} faces of Ni. Using this fact, suitable synthetic conditions for cubic and spherical Ni particles could be derived. It was confirmed that high and low reduction rate favor respectively spherical and cubic shapes during CVD.



ID-333

## Change in the phase composition of the carbon material during mechano-chemical synthesis

*I. Zherebcov, L. Savina, V. Savin, V. Chaika, A. Osadchy, M. Rybin*

In recent decades, many researchers are looking for new properties and their applications of carbon materials. But the mechanism of structural-phase changes in the production of new materials by various methods is not sufficiently studied. The paper analyzes the structural and phase changes in the mechanochemical treatment (MCT) of graphite in the high-energy mill  $E_{max}$ . At the initial stage, the graphite was crushed for 1 hour at a frequency of 1000 rpm, and further processing was performed at a frequency of 2000 rpm for 10 50 minutes with a stop after every 10 minutes per day.

X-ray studies revealed 9 phases in the original powder. At MCT up to 50 minutes, a non-linear change in the percentage of phase composition occurs. Several regularities have been established:

- with a decrease in the 2H Hexagonal phase content and a decrease in carbon monoxide content, the Hexagonal phase content of P63mc and P63/mmc increases;
- with an increase in the 2H Hexagonal phase content and an increase in carbon monoxide content, the content of Hexagonal phases P63mc and P63/mmc and non-Hexagonal such as Orthorhombic Fmmm and Rhombo.R.axes R-3m decreases;
- along with an increase in the 2H Hexagonal phase, an increase of more than 1% of diamond-like phases such as Orthorhombic Cmmm and Cubic Ia-3 occurs.

Note that diamond-like phases were not detected after 50 minutes of MCT; the particle size of the powder increased, it was suggested that, thanks to the process of enveloping the solid phase with a more plastic phase, the diamond-like phases are hidden and not available to X-ray studies. This assumption is confirmed by chemical methods of analyzing this powder. A component that cannot be etched with sulfuric, nitric or hydrochloric acid, or mixtures of them based on water or alcohols, is not found. This is not characteristic of graphite. Such properties are characteristic for a diamond-like carbon.

So, it is possible to assert that over 40 mines of mechanochemical synthesis bring to receipt of diamond-like phase that does not disintegrate.

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ID-340

**Epitaxial versus polycrystalline shape memory Cu-Al-Ni thin films**

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In this work two different approaches were followed to obtain Cu-Al-Ni thin films with shape memory potential. On the one hand, Cu-Ni/Al multilayers were grown by magnetron sputtering at room temperature. To promote diffusion and martensitic/austenitic phase transformation, the multilayers were subjected to subsequent heat treatment at 700°C and quenched in iced-water. On the other hand, Cu, Al and Ni were co-sputtered onto heated MgO (001) substrates, held at 700°C. Energy-Dispersive X-ray Spectroscopy (EDX), X-ray Diffraction (XRD) and Transmission Electron Microscopy (TEM) analyses were carried out to study the resulting microstructures. In the former method, with the aim to tune the thin film's composition and, consequently, the martensitic transformation temperature, the sputtering time and applied power were adjusted. Accordingly, Cu-14Al-4Ni (wt %) martensitic thin films and Cu-12Al-7Ni austenitic (wt %) thin films were obtained. In situ heating during film growth led to Cu-12Al-7Ni (wt %) austenitic thin films with a (200) textured growth as a result of the epitaxial relationship MgO(001)[100]/Cu-Al-Ni(001)[110]. Resistance versus temperature measurements were carried out to investigate the shape memory behaviour of the austenitic Cu-12Al-7Ni (wt%) thin films. While no signs of martensitic transformation were detected in the quenched multilayered thin films, a trend that might be indicative of thermal hysteresis was encountered for the epitaxially grown thin films. In the present work, the differences in the crystallographic structure and the shape memory behaviour of the Cu-Al-Ni thin films obtained by the two different preparation approaches will be discussed.

ID-344

**Magnetic properties of core/shell manganese oxide nanoparticles before and after degradation in water***A. Omelyanchik<sup>1</sup>, G. Singh<sup>2</sup>, B. Hjelmeland McDonagh<sup>3</sup>, V. Rodionova<sup>1</sup>, D. Fiorani<sup>4</sup>, D. Peddis<sup>4</sup>, S. Laureti<sup>4</sup>*<sup>1</sup> Immanuel Kant Baltic Federal University, 236041, Kaliningrad, Russia<sup>2</sup> Department of Materials Engineering, Norwegian University of Science and Technology (NTNU), 7491, Trondheim, Norway<sup>3</sup> Ugelstad Laboratory, Dept. Of Chemical Engineering, Norwegian University of Science and Technology (NTNU), 7491 Trondheim, Norway<sup>4</sup> Istituto di Struttura della Materia-CNR, 00015 Monterotondo Scalo (RM)

In this work, magnetic properties of L-DOPA stabilized core/shell  $\text{Mn}_3\text{O}_4/\text{MnO}$  nanoparticles were investigated during the process of degradation [1-2]. The as-prepared  $\text{Mn}_3\text{O}_4/\text{MnO}$  core/shell system demonstrates a low temperature magnetization reversal that is strongly affected by the presence of the MnO shell. As results, the finite coercivity slightly above the Curie temperature of the  $\text{Mn}_3\text{O}_4$  phase, the horizontal displacement of the FC-hysteresis loop as well as the existence of a frustrated interfacial region determining the low temperature irreversibility were observed. On the other hand, the magnetic behavior of the aged system is dominated by the presence of  $\text{Mn}_3\text{O}_4$  whose highly anisotropic character (i.e. high coercivity and high magnetization remanence) is attributed to the presence of a large fraction of surface spins. Such result is consistent with the structural evolution, from core/shell to hollow nanoparticles, as shown by TEM observation.

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ID-347

**Synthesis of nanosized Pd-catalysts on activated and Al-Zr-pillared montmorillonite and their catalytic behavior in the isomerization of n-hexane***L. Jumabayeva, N. Zakarina, L. Komashko, G. Akulova*

Palladium nanoparticles deposited on various carriers showed high catalytic activity in hydrogenation, oxidation, isomerization, etc. For the synthesis of palladium sols, we used polyoxometallates formed by the elements of V and VI of the Periodic table that can be represented general formulas  $MmOy X^-$ , where M-Mo, W, V in higher degrees of oxidation. These compounds modify the properties of noble metals and stabilize them in a highly dispersed state.

The purpose of this work is the synthesis of stable, concentrated palladium sols and supported Pd catalysts based on them, and the study of the physicochemical and catalytic properties of Pd catalysts supported on activated and pillared montmorillonite (MM) in the isomerization of n-hexane.

The catalysts were prepared by impregnating the support with aqueous Pd sol solutions, followed by drying, calcining and reduction of the oxides to the metallic state. The metal content in the samples is 0.35 and 0.1 wt. %.

The obtained samples were characterized by the XRD, TEM and TPD  $NH_3$ .

The activity of the samples in the isomerization of n-hexane was investigated in a flow reactor with varying the process temperature in the range 250–400 °C. The process was carried out in a stream of hydrogen, an analysis of products was gas chromatography.

According to the BET analysis, the formation of the columnar Al-Zr-NaHMM structure characterized by the redistribution of pores in size, while the specific surface area of the samples and the total pore volume are increased.

According to electron microscopy data, the concentrated Pd hydrosols are characterized by a uniform distribution of metal particles in size. The preferred particle size is 4.0–5.0 nm. When depositing the sols on the pillared montmorillonite, the size of the palladium particles is persists. Along with the uniformly sized palladium particles, larger particles are identified on the surface, which, according to the microdiffraction data, are the products of interaction of Pd with the carrier:  $Pd_2Si$ ,  $Pd_4Si$ , and  $Pd_5Si$ .

The introduction of Pd-sol in Al-Zr-pillared MM leads to an increase of the isomerization activity of the catalyst and practical suppression of hydrocracking. The total content of isohexanes at 400 °C is 47.0% and that of isoheptanes is 7.5%. Thus, the use of Pd sols stabilized with polyoxometallates for the preparation of light n-alkane isomerization catalysts seems to be a promising direction.

ID-348

**Mesoporous  $\text{CoFe}_2\text{O}_4$  sorbents for  $\text{H}_2\text{S}$  removal at mild temperature***A. Ardu<sup>1</sup>, C. Cara<sup>1</sup>, V. Marnelli<sup>1</sup>, E. Rombi<sup>1</sup>, A. Musinu<sup>1</sup>, C. Cannas<sup>1</sup>*<sup>1</sup> *University of Cagliari*

It is well known that the concentration of hydrogen sulphide ( $\text{H}_2\text{S}$ ) in a raw syngas produced from coal gasified must be lower than 150 ppm to permit its use in power production. Since the seventies, several metal oxide have been proposed as potential and efficient sorbents in a wide range of temperature. Among them, ferric oxides, having high sulphur capacity and excellent regenerability in the range of the mid temperature (300°C - 600°C) resulted very promising sorbents. However, pure active phases, even if nanostructured, suffer from the main drawback of sintering phenomena during the repeated sulphidation and regeneration cycles. Therefore, two main strategies have been followed to overcome this issue: i) the dispersion of the active phase in porous and stable matrices ii) the development of porous active phases. Both approaches should, at least in principle, hamper the sintering of the particles and allow the sorbent to be regenerated. In this context, in this work,  $\text{CoFe}_2\text{O}_4$  in form of mesoporous spherical aggregates of small nanoparticles, has been proposed as sorbent for  $\text{H}_2\text{S}$  removal. Mesoporous  $\text{CoFe}_2\text{O}_4$ , synthesized from a sodium dodecyl sulfate-assisted water-based (1) were used directly, without further treatments, as sorbent for  $\text{H}_2\text{S}$  removal at 300°C and submitted to multi-cycles sulphidation-regeneration tests. The microstructure and morphology of fresh and sulphided  $\text{CoFe}_2\text{O}_4$  sorbent were studied by X-ray diffraction (XRD), transmission electron microscopy (TEM and also in the high resolution mode, HR-TEM) and  $\text{N}_2$ -physisorption techniques to verify the effective modification of the sorbent after the sulphidation treatment. Moreover, the sulphidation and regeneration runs were monitored, studying the outlet gas from the reactor by mass spectrometry, and the obtained sulphur retention capacity (SRC) of the sorbent were compared with commercial samples.

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ID-350

**Effect of short time annealing at Fe  $\alpha/\gamma$  transition on the microstructure of milled Nd<sub>2</sub>Fe<sub>14</sub>B+10wt% $\alpha$ -Fe magnetic nanocomposites***R. Hirian<sup>1</sup>, O. Isnard<sup>2</sup>, V. Pop<sup>1</sup>*<sup>1</sup> Faculty of Physics, Babeş-Bolyai University<sup>2</sup> Institut Néel, CNRS and Université Grenoble Alpes

Magnetic properties of the soft/hard Nd<sub>2</sub>Fe<sub>14</sub>B+10wt% $\alpha$ -Fe nanocomposites, obtained through mechanical milling, are closely linked with the structure and microstructure of both hard and soft magnetic phases. The as-milled powders present a very high defect density. In order to increase the crystallinity of the powders, while also keeping the mean crystallite sizes of both the hard and soft magnetic phases as low as possible, the samples need to be annealed in very well controlled conditions. In previous work rapid annealing for up to 2.5 min at 700, 750 and 800°C has proved to be effective at restoring some of the crystallinity of the hard magnetic phase, while keeping Fe crystallite sizes below 20 nm. This work builds upon these results in two ways: first, increasing rapid annealing temperature and secondly taking advantage of the Fe  $\alpha/\gamma$  transformation by combining heat treatment above 920°C and under 900°C. Annealing for 4 h at 350°C was also performed on some samples before rapid annealing in order to remove milling induced strains. The structure and microstructure of the nanocomposites were studied through XRD and SEM while their magnetic properties were studied using demagnetization curves ( $\pm 10$  T) and dM/dH plots.

ID-355

**The structure of  $\text{VNbO}_5$  ternary oxide compound prepared by extended ball milling of  $\text{V}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  powders followed by thermal ageing at  $650^\circ\text{C}$** *N. Senes<sup>1</sup>, A. Valentoni<sup>1</sup>, G. Mulas<sup>1</sup>, S. Garroni<sup>2</sup>, S. Enzo<sup>1</sup>*<sup>1</sup> University of Sassari<sup>2</sup> University of Burgos

It was recently demonstrated that the ternary oxide  $\text{VNbO}_5$  can be obtained via a solid-state route starting from equimolar mixtures of  $\text{V}_2\text{O}_5$  and  $\text{Nb}_2\text{O}_5$  crystalline powders subjected to ball milling conducting to full amorphization. The further moderate thermal treatment afforded crystallization of the  $\text{VNbO}_5$  phase, which induced remarkable effects on the sorption performance of  $\text{MgH}_2$  system. Particularly, the hydrogen desorption temperature of  $330^\circ\text{C}$  reported for un-doped  $\text{MgH}_2$  sample is lowered to  $235^\circ\text{C}$  after conducting the process in the presence of the  $\text{VNbO}_5$  powdered phase. Further, more than 5 wt% of hydrogen can be absorbed in 5 minutes at  $160^\circ\text{C}$  under 20 bar of hydrogen, which is remarkable compared to the figure of 0.7 wt% achieved for the un-doped system.

The structure of  $\text{VNbO}_5$  previously reported for powders synthesized by sol-gel, was assumed to be isostructural with the  $\text{VTaO}_5$  compound (orthorhombic, space group Pnma) synthesized analogously. The Rietveld refinement carried out on XRD data permitted to locate the atomic species position in the unit cell and to conclude that the structure can be envisaged as a series of inter-connected distorted octahedra and tetrahedra where the oxygen anions are surrounding exclusively niobium and vanadium ions, respectively.

A scrutiny of powder patterns obtained for our ball milled products subjected to moderate thermal treatment, showed the presence of weak unindexed peak profiles that could be included in the fit when the assumed space group symmetry is lowered from Pnma (n. 62 in the IT) to P212121 (n. 19 in the IT). While the qualitative structure description in terms interconnected polyhedra is not changing dramatically, yet the interatomic distance distribution by oxygen atoms surrounding metal atoms is sensibly affected.

Starting from an ab-initio approach using simulated annealing followed by final refinement according to Rietveld, we will draw our conclusions on the true P212121 structure of our  $\text{VNbO}_5$  compound so obtained our ball milling in order to achieve more correct insights and understanding about the observed catalytic behavior for the reported hydrogen storage-and-release properties.

ID-357

**Characterization of montmorillonite based organoclay using an ethoxylated fatty acid as a template***D. Liguori, E. Andreoli de Oliveira, G. José da Silva*<sup>1</sup> *Universidade de Brasília*

Over the past few years, several scientific works have been dedicated to the preparation and study of composite materials that combine rigid components with soft and flexible materials aiming potential applications in biomedicine and materials engineering. In particular, mineral clays have been considered as fundamental components in the preparation of systems for drug encapsulation, removal of contaminants in water and biocompatible materials for implants [1, 2]. In this work, we investigate the incorporation of montmorillonite nanoparticles into a lamellar phase composed of ethoxylated fatty acids (Simulsol M45 – Seppic). The original powder of the clay used in this work is composed of polydisperse nanoparticles with average diameter of 500 nm and 1 nm thick, so we developed a size-sorting protocol aiming to select the smaller ones. Solutions of montmorillonite nanoparticles presents sol and gel phases, the former one, at higher concentrations, exhibit permanent birefringence [3]. The lamellar phase, composed of a regular stack of surfactants separated by a water layer is chosen as a template because the nanoparticles can be incorporated to either the water channel or the bilayer, depending on their character, hydrophilic and hydrophobic, respectively [4]. The confinement is modulated by controlling the water content of the lamellar phase. Since the surfactant is nonionic, the main mechanism involved in the formation of a stable structure is of entropic nature, i.e. thermal fluctuations. Following this strategy, we investigate the ordering of montmorillonite nanoparticles inserted in the lamellar phase by SAXS experiments for a varying amount of w/w of clay.

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ID-361

**Development of novel ultrafine grain Cu metal matrix composites reinforced with Ti-Cu-Co-M (M: Ni, Zr) amorphous-nanocrystalline powder***A. Sycheva<sup>1</sup>, D. Janovszky<sup>1</sup>, F. Kristaly<sup>2</sup>, T. Miko<sup>1</sup>, M. Sveda<sup>1</sup>*<sup>1</sup> *Institute of Physical Metallurgy, Metal Forming and Nanotechnology, University of Miskolc*<sup>2</sup> *Institute of Mineralogy and Geology, University of Miskolc*

Novel ultrafine grain composites of Cu matrix reinforced with 2-50 wt.% of  $\text{Ti}_{48}\text{Cu}_{39.5}\text{Ni}_{10}\text{Co}_{2.5}$  and  $\text{Ti}_{48}\text{Cu}_{39.5}\text{Zr}_{10}\text{Co}_{2.5}$  (at.%) amorphous-nanocrystalline alloy particles have been fabricated by powder metallurgy. The composites showed a homogeneous structure. The characterization of composites was performed by optical and scanning electron microscopy (SEM), X-ray powder diffraction (XRD), micro- and macrohardness, as well as density measurements. After hot-pressing the crystallite size of Cu was smaller than 200 nm and nanocrystalline phases of reinforcing powder were 5-35 nm. Densities of 97-76 % relative to calculated values of consolidated composites were obtained, depending on the reinforcing weight fraction. Additionally, the mechanical properties and electrical resistivity of composites have been investigated. The results reveal that the 0.2% offset compressive yield strength of composites increases by two and five times, with respect to pure Cu matrix, for the composites reinforced with 2 and 50 wt.% of reinforcing particles, respectively. Electrical resistivity increases continuously, with higher values after 30 wt.% of addition. Changes in mechanical and electrical properties were produced by the increase of amorphous-nanocrystalline additive. All the results showed that amorphous-nanocrystalline particles are promising alternative reinforcement materials for Cu-based composites, with significantly improved mechanical properties, which may lead to the development of modern types of composites. As a result, varying the nature and the weight fraction of reinforcing particles one can achieve a good balance between strength and electrical conductivity depending on application field of composites.

ID-374

## Thermogravimetry coupled with evolved gas analysis for nanoparticles characterization

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Nowadays, nanoparticles (NPs) are a fundamental research field covering different applicative and technological possibilities, such as energy (fuel and solar cells), environment (wastewater treatment) and medicine (drug delivery, biomarkers). NPs can be prepared in several methods for example through hydrothermal processes, precipitation or combustion syntheses; generally, all of these methods employ the use of metal-organic precursors, organic additives and solvents. Moreover, for specific use (e.g. drug delivery), a post synthesis functionalization with suitable organic ligands is strictly necessary. Consequently, the final NPs are often composed by an organic moiety due to intentional adding or as unwanted precursors residual. The identification of this organic part constituted a crucial point even if it could be not trivial.

Among the different materials characterization techniques, the thermogravimetry (TG) constitutes a straightforward method capable to quantify residual solvents, organic moieties and impurities. Unfortunately, the technique is not able to discern the different compounds released during the heating. Thus, the coupling with the evolved gas analysis remedies to this lack. In this study we present an overview of the application of the thermal analysis (DTA/TG) coupled with the gas chromatography – mass spectrometry (GC – MS) for the investigation of NPs. In particular, we have successfully exploited this coupled technique for the quantification of the organic ligands bonded on Au – NPs [1], the identification of the stability role of organic ligands in nanoperovskite [2,3], and the quantification of organic residual in multishells magnetic ferrites.

Generally, DTA/TG – GC – MS can be considered a powerful technique with new and wide applicability in the investigation of functionalized NPs and materials characterization.

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ID-379

## Synthesis of $\text{Sr}_2\text{FeMoO}_{6-\delta}$ nanostructures in the anodic alumina matrices by the sol-gel method

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This work presents new nanotechnological approaches of synthesis of system Sr-Fe-Mo-O compounds from colloidal solutions in anodic alumina matrices (AAM). The low aspect ratio nanoporous AAM were formed by multi-step anodizing of aluminium films (1.2  $\mu\text{m}$  thick) in 0.4 mol/dm<sup>3</sup> tartaric acid electrolyte with current density of 6 mA/cm<sup>2</sup> at 185 V. To increase the surface-to-volume ratio, the films were subjected to pore modification in mixture of phosphoric and chromic acids at 323 K during 5 minutes. The matrices thickness was 860 nm with pore diameters of 360 nm. The compound of Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  system were prepared by sol-gel method from colloidal solutions by mixing aqueous solutes of Sr(NO<sub>3</sub>)<sub>2</sub>, Fe(NO<sub>3</sub>)<sub>3</sub>, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>, C<sub>6</sub>H<sub>8</sub>O<sub>7</sub> and (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>. The formed gel was deposit to the AAM by centrifugation with followed by three-step structure annealing: at T = 373-473 K for 2 hours to dry the solution; at pO<sub>2</sub> = 0.21×10<sup>5</sup> Pa and T = 773 K for 8 hours to form distribute the Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  film; and at T = 1123 K by means of polythermic approach in gas mixture (5% H<sub>2</sub>/95% Ar) for 10 hours to obtain Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  with structural ordering of Fe<sup>3+</sup> and Mo<sup>5+</sup> cations. We investigated the correlation between the citrate-gel synthesis conditions and AAM microstructure, phase transformations and magnetic properties of synthesized films. The nanostructured compounds during Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  crystallization proceeds through number of parallel chemical reactions that lead to several phase transformation processes. The microstructure, elemental composition of nanostructured ceramics and their magnetic characteristics have been researched. In the energy dispersive X-ray spectrum of Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  we detected elements that belong to the substrate with the AAM – Al (1.432 eV), O (0.56 eV), Si (1.77 eV) – and composite Sr<sub>2</sub>FeMoO<sub>6- $\delta$</sub>  synthesized in the pores – Fe (0.637 eV, 6.4 eV, 7.05 eV), Sr (1.82 eV), Mo (2.32 eV). The weight ratio of elements in the composition was 23.34%- Fe, 58.96%- Sr and 17.70%- Mo, and atomic ratio was 32.77%- Fe, 52.76%- Sr and 14.47%- Mo. According to results of magnetization temperature dependence investigations in nanostructured compounds of system Sr-Fe-Mo-O, a metastable superparamagnetic state was established at T < 19 K in low-dimensional grains. It is shown that the use of porous matrices has allowed creating regular arrays of strontium ferromolybdate nanostructures with more microstructural and magnetic homogeneity and enhanced properties.

ID-386

**Pulsed laser deposition of conductive Zn(O,S) thin films for optoelectronics***S. Bereznev<sup>1</sup>, H. Kocharyan<sup>2</sup>, O. Volobujeva<sup>3</sup>*<sup>1</sup> *Tallinn University of Technology, Department of Materials and Environmental Technology*<sup>2</sup> *Department of Mechanical Engineering, Worcester Polytechnic Institute*<sup>3</sup> *Tallinn University of Technology, Department of Materials and Environmental Science*

Zinc oxysulfide Zn(O,S) is one of the prospective materials for substitution of conventional CdS buffer layer in complete optoelectronic devices due to its optimal bandgap and low toxicity [1,2]. In present work Zn(O,S) thin films have been prepared by one-step pulsed laser deposition (PLD) technique. The films with a thickness of 650 nm were deposited onto the FTO/glass substrates at different substrate temperatures from room temperature to 400°C. Zn(O,S) layers were characterized by means of scanning electron microscopy, energy dispersive spectroscopy, Raman, X-ray diffraction, Uv-Vis spectroscopy and Van der Pauw technique. It was found, that obtained Zn(O,S) layers are mainly polycrystalline, highly uniform, transparent, electrically conductive and demonstrate good adhesion to the FTO/glass substrates. In addition, we show that elemental composition of PLD Zn(O,S) films depends on the substrate temperature. For the first time high quality conductive Zn(O,S) layers were prepared by one stage PLD in high vacuum at relatively low temperatures (100 and 200°C) without any post treatment. The properties of prepared Zn(O,S) films suggest that these films can be applied as buffer layer in optoelectronic devices.

**ID-395****Synthesis of Ni-Ti coatings on different metallic substrates by mechanical alloying and subsequent laser treatment**

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In this work, we proposed a novel approach to deposit Ni-Ti intermetallic coating of about 50 - 70  $\mu\text{m}$  thickness on the surface of Ni, Al, Ti, and hypo eutectoid steel substrates by mechanical alloying (MA) using vibratory ball mill with subsequent laser treatment. The microstructure and phase composition of the obtained coatings, before and after laser treatment, was analyzed using X-Ray diffraction and Scanning electron microscopy. Micro-hardness of the samples was measured using Vickers hardness tester and it was observed that Ni-Ti coating improves the hardness of the sample significantly. Best results were found in case of Ti substrate, where we found rather large amount of the Ni-Ti intermetallic compounds, after laser treatment at 3.4  $\text{J}/\text{mm}^2$ , but, it was not a single NiTi intermetallic compound single-phase.

This work was partly supported by the Ministry of Education and Science of the Russian Federation within the framework of the Increase Competitiveness Program of MISiS and from the grant of the Russian Ministry of Education and Science, contract No. 11.1934.2017/ПЧ.

ID-396

**Cellulose fibers from palm fibers coated by zirconium oxychloride***D. Mulinari, L. Martins, N. Zanini, W. Paixão**Universidade do Estado do Rio de Janeiro*

Surface modification of natural fibers has been carried out with many metal oxides. Depending upon the metal oxide, the use has related to a specific application. Experimental methodology of the coating process depends on the cellulose morphology, either fiber or membrane that is obtained. As a fiber, the treatment of cellulose with a precursor reagent can be in either an aqueous or non-aqueous solvent. In this work, cellulose fibers from Australian king palm were bleached and modified by zirconium oxychloride in situ. The chemically modified cellulose fibers were compared to those of bleached ones. Cellulose fibers were modified with  $ZrO_2 \cdot nH_2O$  nanoparticles through the use of zirconium oxychloride in acidic medium in the presence of cellulose fibers using ammonium solution as the precipitating agent. The spatial distribution characterization of hydrous zirconium oxide on cellulose fibers was evaluated by techniques Scanning electron microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared (FTIR) and thermogravimetric analysis (TG) were also used to characterize the nanocomposite. Results indicated that  $ZrO_2 \cdot nH_2O$  nanoparticles of about 30–80 nm diameter deposited on cellulose fibers were heterogeneously dispersed.

ID-401

**Realization of carbon nanotube-based stretchable electronic devices and applications**

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Single wall carbon nanotube based conductors, firmly self-grafted on different polymer films, are assembled aiming at a simple technology for flexible and stretchable electronic devices. Electrical characterization of both unstretched and strongly stretched conductors is provided, while an insight of the mechanisms of strong adhesion to the polymer is obtained by scanning electron microscopy of the surface composite. The demonstration of a technological application of such stretchable circuitry is provided, whereby the electrical functionality of a carbon nanotube-based 6-sensor (electrode) grid is used to record subdural electrocorticograms in freely-moving rats over approximately three months.

ID-417

**Hydrothermal methods with microwaves, rotavapor to obtain  $V_2O_5$ - $WO_3/TiO_2$ /Au impregnated with Cs, Li and with Cs-Li***J.A. Carmona-Garcia<sup>1</sup>, I. Mejia Centeno<sup>2</sup>, L.A. Garcia-Serrano<sup>1</sup>*<sup>1</sup> Instituto Politécnico Nacional<sup>2</sup> Instituto Mexicano del Petróleo

The deterioration of air quality in large cities is a complex problem to face successfully and even more to solve. However, we believe that the massive use of the selective catalytic reduction system in vehicles with diesel engines and in fixed sources, as a new measure of NOx emission control, could contribute to improving air quality. In this work he focuses on the preparation of  $V_2O_5$ - $WO_3/TiO_2$ /Au impregnated with Cs, Li and with Cs-Li. By means of hydrothermal treatment with microwaves, rotavapor was characterized morphologically, structurally, thermally and techniques to determine the type of basic sites. In all cases the anionic laminar material impregnated with Ce, prepared by the microwave method, was the most active material. The material impregnated with Li, prepared by coprecipitation (rotavapor) is the second most active material, while the impregnated with CeLi, prepared by the same method.

Therefore, where the synthesis method seems to influence is in the case of It is the third most active material, except in the reaction of benzaldehyde with ethyl malonate (pKa = 13.3), which are reversed papers. The fourth most active material was impregnated with CeLi by a rotavapor method, followed by the material impregnated with CeLi by this same method. Finally, the material with less activity was impregnated with Ce, by the rotavapor method, except in the reaction of benzaldehyde with ethyl malonate in which it had approximately the same activity as the material impregnated with Celi by this same method. All materials decreased their activity by increasing the pKa of the methylene group contained in the malonic esters, since in order to abstract the protons from these, sites with greater basic strength were required.

With this analysis you can conclude that the material with the highest number of active sites of strong basic strengths is the one impregnated with Ce by the microwave method, although its conversion was decreasing as the pKa of the methylenic group of the malonic ones increased. it decreased more than 15% approximately, reaching a good conversion to the product of Knoevenagel condensation. The material with less basicity was that impregnated with Ce by the rotavapor method



ID-424

**Architecting layer by layer hybrid materials on titanium for painless implantation***S. Fatimah, Y. Ko**Yeungnam University*

Commercially pure titanium grade 4 was modified using green plasma electrolysis followed by impregnation of organic compounds to grow hybrid coatings possessing high roughness and area of the surface for biomaterials application. The surface roughness of hybrid coatings on titanium was controlled by the electrolyte parameter and the selection of organic compounds loaded after plasma electrolysis.  $K_3PO_4$  and  $K_4P_2O_7$  were selected as the electrolyte components to fabricate porous and rough inorganic layer. Hydroxyapatite (HA) and octacalcium phosphate (OCP) were loaded into the inorganic layer to form a hybrid layer and to promote bioactivity. The drug delivery characteristics of biomaterials were often considered in order to incorporate a dose of medicine onto the surface of biomaterials to reduce the inflammation during implantation. This characteristic was analyzed through albumin release for 48h. The morphology, cross-section and chemical composition of the samples were investigated using scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), X-ray diffraction (XRD) and Raman spectroscopy. The surface roughness of the oxide layers was measured by atomic force microscopy (AFM), whilst corrosion behavior of the hybrid layer was examined by potentiodynamic polarization in Ringer's. The electrochemical properties, as well as the drug delivery characteristics, would be discussed by taking the surface morphology, crystallinity, and the composition of the hybrid layer into account.

ID-434

**Synthesis and characterization of a new photocatalyst based on TiO<sub>2</sub> nanoparticles supported on magnetic materials from iron and steel industrial waste***M. Ferretti<sup>1</sup>, V. Caratto<sup>1</sup>, S. Alberti<sup>1</sup>, D. Peddis<sup>2</sup>, C. Belviso<sup>3</sup>, M. Sturini<sup>4</sup>, F. Maraschi<sup>4</sup>*<sup>1</sup> Department of Chemistry and Industrial Chemistry, University of Genoa<sup>2</sup> ISM – CNR<sup>3</sup> Istituto di metodologie per l'analisi ambientale - CNR<sup>4</sup> Department of Chemistry, University of Pavia

Photocatalysis can be exploited in numerous applications for the solution of emerging environmental problems such as the pollutants removal from aqueous media or the environment preservation from bacterial contamination [1]. Titanium dioxide (TiO<sub>2</sub>) based devices have been deeply investigated during the last decades, although it suffers of two important drawbacks, the low solar sensitivity and troubles related to its recovery. In the current work a new catalyst has been developed consisting of nanometric TiO<sub>2</sub> supported on materials obtained from the treatment of industrial wastes (fly ash and/or fly ash mixed with red mud) containing iron and showing potential magnetic properties (MaM) [2]. MaM materials represent an excellent example of circular economy, in fact the industrial waste is converted into a product with high technological value that can be used, together with the photocatalyst, for the degradation of emerging pollutants from aqueous media [3]. In particular, TiO<sub>2</sub> nanoparticles are synthesized through a sol-gel synthesis and the gel obtained is dried in an oven at 105°C for 12 hours. Then photocatalyst powders are mixed in an aqueous solution with MaM by ultrasounds, using different pH conditions: 0.1 M HNO<sub>3</sub> for the acidic solution while 0.1 M NaOH for the alkaline one. The different suspensions are finally subjected to two different thermal treatments (90°C under vacuum or 200°C). The synthesized devices are fully characterized by means of XRD, SEM and BET analyses and their photocatalytic activity is evaluated through the abatement of methylene blue solutions, according to the ISO norm 10678:2010. The most efficient photocatalyst (TiO<sub>2</sub>+Fly Ash) will be tested on a fluoroquinolone antibiotic solution in order to prove its efficiency on emerging contaminants abatement.

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ID-435

**Tailoring nucleation and stress magnitude during surfactant-mediated metallic film growth***C. Furgeaud<sup>1</sup>, L. Simonot<sup>2</sup>, A. Michel<sup>2</sup>, D. Babonneau<sup>2</sup>, S. Camelio<sup>2</sup>, C. Mastail<sup>2</sup>, G. Abadias<sup>4</sup>*<sup>1</sup> Institut Pprime, CNRS-Université de Poitiers – ENSMA<sup>2</sup> Institut Pprime, Département de Physique et Mécanique des Matériaux,

The growth of high-mobility metals on weakly interacting substrates (e.g. SiO<sub>2</sub>) proceeds in a 3D mode, while exhibiting a complex stress evolution that is indicative of the successive stages such as nucleation of isolated islands, coalescence and formation of a continuous film. The control of island size and shape in the early stages of growth is of prime importance for many applications ranging from architectural glazing to plasmonics, or even to catalysis, as the characteristic length scales (as the lateral grain size) and physical attributes of ultrathin films are mostly set-in during the coalescence stage.

In this field of investigations, we focus on the growth of Cu thin films on oxidized Si substrates. The effect of Ge alloying on the growth morphology and intrinsic stress evolution during Cu deposition is investigated using in situ and real time diagnostics, complemented by ex situ microstructural characterization. The stress and reflectance evolutions are measured in real-time during growth by coupling simultaneously multiplebeam optical stress sensor (MOSS) and surface differential reflectance spectroscopy (SDRS). We identify the percolation thickness from in situ electrical resistivity measurements [1], while the onset of film continuity is determined from the maximum tensile force using a multiple beam optical stress sensor [2]. Complementary analyses using atomic force and transmission electron microscopy are employed to obtain information on the growth morphology, surface roughness, texture change and grain size.

Cu<sub>1-x</sub>Ge<sub>x</sub> alloys with x up to 0.15 were sputter-deposited at room temperature on native oxide covered Si substrates. All films exhibit a typical compressive-tensile-compressive stress behavior, characteristic of the distinct stages of a Volmer-Weber growth; however, it is revealed that the Ge content plays a decisive role on the nucleation and coalescence stages. This results in a grain size refinement and development of increased compressive stress for Ge additions up to x=0.07. At higher Ge contents, the strong chemical affinity between Cu and Ge atoms leads to a germanide compound formation and even larger compressive stress.

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ID-440

**Room temperature consolidation of pure magnesium/aluminum composite by high pressure torsion***M.M. de Castro<sup>1</sup>, S. Sabbaghianrad<sup>2</sup>, E.M. Mazzer<sup>1</sup>, A.C. Isaac Neta<sup>1</sup>, R.B.Figueiredo<sup>1</sup>, T.G. Langdon<sup>3</sup>*<sup>1</sup> *Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais*<sup>2</sup> *Departments of Aerospace and Mechanical Engineering & Materials Science, University of Southern California*<sup>3</sup> *Materials Research Group, Faculty of Engineering and the Environment, University of Southampton*

High pressure torsion (HPT) is a well-known technique for processing nanostructured materials. Pure metals such as Al, Cu and Mg, and several alloys have been processed by HPT leading to ultra- fine microstructures. During the past decade, HPT has attracted the attention of researchers as a powder and bulk consolidation method. Dense and refined samples have been obtained, but only a small amount of research was dedicated to the mixture of different metals and alloys. Therefore, the present work used HPT in order to mix and consolidate pure magnesium and pure aluminum at room temperature. Samples in the form of half discs of the different materials were processed at 6 GPa for different numbers of turns. Scanning electron microscopy showed an increase in the surface areas between the different phases with increasing numbers of turns. Nevertheless, the thickness of the phases decreased. Transmission electron microscopy showed that significant grain refinement takes place within each phase and there is no evidence of intermetallic formation in the boundaries between the phases, as would be expected from the Al-Mg equilibrium phase diagram. The results indicate that high pressure torsion is an effective procedure for mixing metallic phases at low temperatures.

ID-445

**Optical properties of nanocrystalline/amorphous TiO<sub>2</sub> thin film deposited by rf plasma magnetron sputtering***A.A. El-Moula, M. Raaif**Physics Department, Faculty of Science, Sohag University, Egypt*

This work is a part of serious experimental efforts established on constructing multilayers based on TiO<sub>2</sub> for industrial use in optical devices. Recognizing the structure and optical features of TiO<sub>2</sub> single layer is very significant in designing optical devices and in constructing multilayers based on TiO<sub>2</sub> layer for probable industrial requests. In this regard, rf plasma magnetron sputtering was employed to prepare TiO<sub>2</sub> thin film on glass substrates. The effect of oxygen ratios % with respect to argon on the optical characteristics of TiO<sub>2</sub> thin film was studied. Structural studies revealed the transition from crystallization to amorphous nature of TiO<sub>2</sub> films with increasing the oxygen ratios. All TiO<sub>2</sub> thin films were transparent in the visible zone and the transmittance of TiO<sub>2</sub> films increased with increasing the O<sub>2</sub> ratios. The estimated energy gap of TiO<sub>2</sub> thin films increased from 3.25 eV to 3.37 eV with increasing the oxygen ratios. However, the refractive index decreased with increasing the oxygen ratios. Moreover, diverse optical constants like optical conductivity ( $\sigma_{opt}$ ), dielectric constants ( $\epsilon_i$  and  $\epsilon_r$ ), Urbach energy ( $E_u$ ), the dispersion energy ( $E_d$ ) and single oscillator energy ( $E_o$ ) have been explored and discussed.

ID-454

**Studies on  $\text{CoFe}_2\text{O}_4@\text{TiO}_2:\text{Tb}$  magnetic recoverable nanocomposites with enhanced photocatalytic activity***M. Stefan<sup>1</sup>, O. Pana<sup>1</sup>, A. Popa<sup>1</sup>, D. Toloman<sup>1</sup>, T.D. Silipas<sup>1</sup>, C. Leostean<sup>1</sup>, S. Macavej<sup>1</sup>, L. Barbu-Tudoran<sup>1</sup>**<sup>1</sup> National Institute for Research and Development of Isotopic and Molecular Technologies*

Photocatalytic technology represents the most important routes for removing organic pollutants from wastewater. One major challenge in photocatalysis applications is the separation and recovery of nanosized photocatalyst particles from the treated water. In this regard, the use of magnetically separable composite photocatalysts represents a possible approach for wastewaters treatment.

The purpose of the present work is to study the influence of synthesis conditions on morpho-structural, optical, magnetic and photocatalytic properties of  $\text{CoFe}_2\text{O}_4@\text{TiO}_2:\text{Tb}$  composite nanoparticles.

The  $\text{CoFe}_2\text{O}_4@\text{TiO}_2:\text{Tb}$  core-shell nanoparticles were prepared by a two-stage process: first  $\text{CoFe}_2\text{O}_4$  nanoparticles were obtained by chemical coprecipitation method and then they were coated with terbium doped  $\text{TiO}_2$  nanocrystallites by a sol-gel process. Finally, the samples were calcined in order to get the anatase phase of titanium dioxide.

The composites were characterized by using X-Ray Diffraction (XRD), Transmission Electron Microscopy (TEM and high resolution-TEM), X-ray Photoelectrons Spectroscopy (XPS), FT-IR and Raman Spectroscopy. Also, magnetization behavior and photocatalytic properties were investigated. Electron Spin Resonance (ESR) experiment coupled with spin-trapping technique was carried out in order to evidence the production of reactive radical groups at the solid-liquid interface of  $\text{TiO}_2$ .

The photocatalytic tests demonstrated that the composite nanoparticles exhibit good photocatalytic activity toward the degradation of RhB solution. The high photocatalytic activity of  $\text{CoFe}_2\text{O}_4@\text{TiO}_2:\text{Tb}$  composites can be attributed to the synergetic effects of different components from the composite nanostructures.

**Acknowledgments:** Financial support from the Romanian Ministry of Research and Innovation, Core Programme, Project PN18-03 02 03 is gratefully acknowledged.

ID-455

**Influence of PVP on photocatalytic activity of SnO<sub>2</sub>-TiO<sub>2</sub> composite nanoparticles***D. Toloman, O. Pana, M. Stefan, A. Popa, T. Danut Silipas, C. Leostean, S. Macavei, L. Barbu-Tudoran**National Institute for Research and Development of Isotopic and Molecular Technologies*

In this work, efficient SnO<sub>2</sub>-TiO<sub>2</sub> composite photocatalyst nanoparticles were prepared by seed mediated growth of TiO<sub>2</sub> nanoparticles onto the surface of pre-formed both uncapped and polyvinylpyrrolidone (PVP) capped SnO<sub>2</sub> nanoparticles. The influence of PVP amount on the structural, compositional, morphological and photocatalytic properties was study.

Their characteristics were evaluated by X-ray powder diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS). All synthesized composite nanoparticles contain the same amount of SnO<sub>2</sub> and anatase/rutile TiO<sub>2</sub> in different proportions. The results show that the amount of PVP used in preparation influences the SnO<sub>2</sub> grain sizes and plays an important role in phase stabilization of TiO<sub>2</sub> crystallites. TEM investigations revealed the presence of polyhedral and uniform size nanoparticles with limited aggregation. The particle size distribution is ranging between 10 and 20 nm. By XPS it was evidenced the qualitative composition of samples and the corresponding oxidation states. The photocatalytic activity was evaluated by using a Rhodamine B dye solution under visible light irradiation. Additionally, Electron Spin Resonance (ESR) experiments coupled with spin-trapping technique were carried out to make evidence of reactive radical groups production at the solid-liquid interface during the photocatalytic process.

Acknowledgements: Financial support from the Romanian Ministry of Research and Innovation, Core Programme, Project PN18-03 02 03 is gratefully acknowledged.

ID-463

**Structural, compositional and magnetic characterization of  $\text{MeFe}_2\text{O}_4$ /( $\text{Me}=\text{Fe}$ ,  $\text{Ni}$ ,  $\text{FeNi}$ ) nanocomposites**

C. Leostean, O. Pana, M. Stefan, D. Toloman, A. Popa, S. Macavei, T.D. Silipas, S. Gutoiu<sup>1</sup> L. Barbu Tudoran

National Institute for Research and Development of Isotopic and Molecular Technologies

The magnetic cores with high magnetic properties and high electrical resistivity are required in many AC applications, in order to have a good energy conversion with reduce energy losses. The classical soft magnetic materials are alloys and ferrites. Soft ferrites have a high electrical resistivity, being applicable in high frequencies field, but theirs disadvantage are a low permeability and remanence. In the same time the transition metals (Fe, Ni and theirs alloys) have high permeability and higher induction then ferrites. Nickel ferrite is a promising material but the usual reported saturation magnetization is limited to 60 emu/g. This work report wet chemical preparation as well as the structural, compositional and magnetic characterizations of  $\text{MeFe}_2\text{O}_4$ /( $\text{Me}=\text{Fe}$ , Ni, FeNi) nanocomposites. First  $\text{NiFe}_2\text{O}_4$  nanoparticles were obtained by the precipitation method followed by a 6000 °C calcination. In the next step the preformed  $\text{NiFe}_2\text{O}_4$  were covered with nanocrystalline  $\text{Fe}_3\text{O}_4$  by also using the precipitation method. Finally, the  $\text{NiFe}_2\text{O}_4/\text{Fe}_3\text{O}_4$  composite was thermally treated at 6000 °C in a reducing atmosphere mixture (90%Ar+10%H<sub>2</sub>). The properties of the composites were investigated by TEM, HRTEM, XRD, XPS and magnetization measurements. Different samples with  $\text{NiFe}_2\text{O}_4$ :  $\text{Fe}_3\text{O}_4$  molar ratios of 1:0.5, 1:0.33 and 1:0.25 were prepared. XRD showed that in the initially samples the crystallite sizes are in the range of 7-9 nm for both ferrite and magnetite. After annealing in reducing atmosphere the crystallite sizes increased (up to 50nm) while remaining in the nanoscale range. The final composition of the samples showed a multicomponent system consisting of Ni ferrite, FeNi alloy, Fe(0) and a mixture of iron oxides. The thermally treated samples show significantly increased saturation magnetization (115-168 emu/g) compared to the initial composite (53 emu/g). The coercive field slightly increased up to 94 Oe from 10 Oe. The magnetic behavior of these systems was correlated with the preparation conditions as well as with structural and compositional sample analysis. These properties are adequate for the mentioned applications.

Funding: The authors would like to express appreciation for the financial support to the Romanian UE- FISCDI through project no. 116PED/2017.



ID-467

**The coarsening and formation rate of dispersoids in a ODS Cu alloy with  $\text{Cr}_2\text{O}_3$  produced by the cryogenic milling**

S.J. Hwang

Daejin University

Cu nanocrystalline (nc-Cu) with  $\text{Cr}_2\text{O}_3$  dispersoid (~4 vol. %) was successfully made by simple reactive cryogenic-milling at 210 K with a mixture of pure Cu,  $\text{Cu}_2\text{O}$ , and Cr powder. The vacuum hot pressing (HP) was performed at 1123 K and 50 MPa for 2h to consolidate the milled powder for further analysis. TEM (Transmission Electron Microscopy) work revealed that the HPed materials were comprised with a mixture of the nc-Cu and homogeneous distribution of  $\text{Cr}_2\text{O}_3$  dispersoids. The microstructure and Vickers hardness of as-milled powder and consolidated materials were characterized by standard metallographic techniques. The grain size of the Cu was measured using Scherrer's formula (XRD) and TEM observation; the  $\text{Cr}_2\text{O}_3$  dispersoid size was estimated from the HADDF (High Angle Annular Dark Field) images and element mapping by STEM-EDS (Scanning Transmission Electron Microscopy-Energy Dispersive Spectroscopy) works. The formation kinetics and coarsening of the dispersoids were discussed in terms of the relationship between the microstructure and hardness value, using XRD, TEM, and thermodynamic calculation.

ID-472

**Formation of inorganic layer on  $Ti_6Al_4V$  with different microstructural constituents via plasma electrolytic oxidation***N. Nashrah<sup>1</sup>, K. Choi<sup>2</sup>, Y. Gun Ko<sup>1</sup>*<sup>1</sup> *Yeungnam University*<sup>2</sup> *MST, Gyeongsan 38541, Republic of Korea*

Plasma electrolytic oxidation coatings were fabricated on  $Ti_6Al_4V$  with different morphologies to investigate the effect of microstructural constituents on the coating behavior. The prior heat treatment was carried out at 1338 K 1 h and 1223 K 2 h followed by furnace cooling, which generated equiaxed and widmanstätten microstructures, respectively. The coating process was performed in alkaline-silicate-phosphate base electrolyte employing AC current with fixed current density of 100 mA/cm<sup>2</sup>. The widmanstätten sample exhibited lower breakdown voltage than that of equiaxed sample. Microstructural observations investigated in different stages of the coating formation revealed that plasma discharges formed on the surface of widmanstätten sample was likely to be more uniform due to the distinctive occurrences of initial passive film formation. Accordingly, the oxide layer in widmanstätten sample would tend to be thicker and less porous than that in equiaxed sample, which was confirmed by potentiodynamic polarization test. In addition, the corrosion resistance of the widmanstätten sample was higher as compared to the equiaxed one. Consequently, the interplay between microstructure and electrochemical properties could be elaborated to get a sound understanding of inorganic layer formation on titanium alloys.

ID-480

**Reaction synthesis of TiFe compound from ball milled TiH<sub>2</sub> and Fe mixture: an easy way to produce nanostructured active material for hydrogen storage***R. Bolsoni Falcão, C. José da Rocha, R.M. Leal Neto*

IPEN

TiFe intermetallic compound has been normally produced by mechanical alloying through high energy ball milling of titanium (Ti) and iron (Fe) powder mixtures in order to improve their properties concerning hydrogen storage (absorption and desorption). Several authors associated this improvement with formation of nanostructures during the milling process (nanocrystalline TiFe). However earlier attempts of present authors to synthesize TiFe by this route (in a shaker mill) have failed due to a strong sticking (cold welding) of both Ti and Fe powders (mainly to the vial), preventing mechanical alloying to succeed. In this work TiFe was produced by high-energy ball milling of TiH<sub>2</sub> and Fe powders, followed by heating under vacuum. TiH<sub>2</sub> was used instead of Ti in order to avoid the strong particles adhesion to grinding balls and vial walls. Mixtures of TiH<sub>2</sub> and Fe powders were drymilled in a planetary mill for times ranging from 5 to 40 hours. The amount of sample, number and diameter of the balls were kept constant in all experiments. After milling, samples were heated under dynamic high-vacuum for the synthesis reaction at 600 °C. As-milled and heat-treated materials were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and differential thermal analysis (DTA). The mean crystallite sizes and microstrains were determined by XRD line profile analysis using the Warren-Averbach method. As-milled materials presented only Fe and TiH<sub>2</sub> phases. TiH<sub>2</sub> was effective for providing low adherence of the powders during milling, with yields ranging from 90 to 95 wt%. Nanostructured TiFe compound was formed after the reaction and could absorb hydrogen (at 2MPa) on cooling near room temperature, without thermal activation cycles. The amount of hydrogen absorbed/desorbed by samples was determined by automated Sievert's apparatus, under constant hydrogen flow rate of 9 mL/min (dynamic measurements). Samples milled for shorter times (mainly for 10 hours) could absorb hydrogen for the first time more easily and with better kinetics. However, the samples milled for longer times (25 and 40 hours) shown better results in terms of reversible and storage capacities.

ID-484

## Synthesis and preparation bismuth ferrite nanoparticles for biomedical applications

*D. Kalganov, I.V. Bychkov, A.P. Anzulevich*

*Chelyabinsk State University*

Nanodispersed suspensions of magnetic materials are widely used as contrast agent (or contrast medium) in the diagnosis of diseases by magnetic resonance imaging and ultrasound [1]. A promising field of application of magnetic materials is the preparation of drugs for local hyperthermia. Using for these purposes substances that have pronounced magnetic and electrical properties - multiferroics - will enable non-invasive control of the distribution of the agent in the body by means of external magnetic fields, with high accuracy control of temperature and uniformity of heating in microwave hyperthermia. In addition, the presence of effects associated with changes in the charge of the surface of nanoparticles will also allow to control the activation of drugs and the mechanism of their interaction with target cells [2].

In the present work, powder samples of single-phase multiferroic nanoparticles  $\text{Bi}_{1-x}\text{La}_x\text{FeO}_3$  and  $\text{Bi}_{0,9-x}\text{La}_{0,1}\text{Pr}_x\text{FeO}_3$  were obtained by the citrate-nitrate method (Pechini method), where  $0 > x \geq 0.1$ . For subsequent biomedical research in the live tissue model, the chemically and biologically inert  $\text{SiO}_2$  shell was created on the surface of the nanoparticles obtained.

The phase composition of the samples was determined by X-ray diffraction analysis in the range of angles  $2\theta = 20^\circ - 50^\circ$  in steps of  $0.05^\circ$  on a DRON-3M diffractometer ( $\text{CuK}\alpha$  radiation). The data obtained indicate a low content of the impurity phases  $\text{Bi}_2\text{Fe}_4\text{O}_9$  and  $\text{Bi}_{25}\text{FeO}_{39}$  (ICDD JCPDS file), rhombohedral, and orthorhombic distorted crystal structure. The morphology and particle size were determined by scanning electron microscopy (JEOL-6510, Japan). Average particle size of sample of composition  $\text{Bi}_{0,8}\text{La}_{0,1}\text{Pr}_{0,1}\text{FeO}_3$  about  $1 \mu\text{m}$  and silicate microparticles with a core of a multiferroic have diameter of  $20\text{-}50 \mu\text{m}$ .

[1] M.A. Abakumov, N.F. Grinenko, V.P. Baklaushev, T.O. Sandalova, N.V. Nukolova, A.V. Semyonova, M. Sokol'Ski-Papkov, H. Vishvasrao, A.V. Kabanov, V.P. Chekhonin. Bulletin of Experimental Biology and Medicine., 153, 1, 89-93 (2012).

[2] T. Ibelli, S. Templeton, N. Levi-Polyachenko. International Journal of Hyperthermia., 34, 2, 144- 156 (2018).

ID-487

**Green synthesis of Zinc Oxide nanoparticles using natural extracts***P. Luque Morales<sup>1</sup>, C. Soto Robles<sup>1</sup>, O. Nava Olivas<sup>1</sup>, A. Vilchis Nestor<sup>2</sup>, A. Castro Beltran<sup>3</sup>*<sup>1</sup> *Universidad Autonoma de Baja California*<sup>2</sup> *Universidad Autonoma del Estado de Mexico*<sup>3</sup> *Universidad Autonoma de Sinaloa*

This work presents a study on the effects of different natural extracts in the green synthesis of zinc oxide (ZnO), and its application as a photocatalyst. Zinc nitrate was used as the zinc source while the different natural extract was used as a reductant. The materials were characterized through X-Ray Diffraction (XRD), High-Resolution Transmission Electron Microscopy (HRTEM), and Ultra Violet- to-Visible spectroscopy (UV-Vis). The diffraction patterns of the ZnO samples showed the wurtzite crystalline phase. The morphology of the material showed that varying the amount of extract during synthesis made variations in particle size and shape distribution. The band gap values were around of 3.2 and 3.3 eV. The photocatalytic properties of the ZnO were evaluated through methylene blue (MB) degradation where the sample presented 90% dye degradation in 150 minutes.

**Tuesday 3 July afternoon - 17:30/18:30**

Poster Session 2

**POROUS MATERIALS**

Chair: L. Ruggiero, A. Del Tedesco

ID-33

**Activated carbon from agroindustrial wastes for heavy metal contaminated water treatment**

Á. Aguilar<sup>1</sup>, J. A. L. Correa<sup>1</sup>, A. M. Torres Huerta<sup>1</sup>, M. A. Domínguez Crespo<sup>1</sup>

<sup>1</sup> Instituto Politécnico Nacional

In this work, agroindustrial wastes such as sugar cane bagasse (SCB) and orange peel (OP) were used for obtaining activated carbon (AC), which will be used as sorbent material for wastewater treatment. Preparation of the sorbent material consisted of two activations. Firstly, physical activation at high temperature of 400°C for raw material decomposition; for the second activation, an agent was used: phosphoric acid of 45 wt.%, at temperature of 500°C. The chemical and morphological characteristics of these adsorbent materials such as porosity, functional groups, high surface area are high significance for removing contaminants from wastewater. The adsorbent was characterized using scanning electron microscopy (SEM), for studying the morphology of modified activated carbon, the functional groups, before and after the activation of carbon, were identified by FT-IR analysis; the specific surface area and pore size were measured using (BET) method with Automated Gas Sorption; activated carbon structural changes were studied by X-ray diffraction. Finally, by thermogravimetry (TGA) was obtained information about the behavior thermal of raw material and activated carbon.

Keywords: Activated carbon, agro-industrial wastes, bioadsorption, heavy metal ions, contaminated water.

## ID-63

**Pore characteristics of nickel, iron and cobalt impregnated on SBA-15**

*H. L. Chiang<sup>1</sup>, T. Y. Lee<sup>1</sup>*

<sup>1</sup> *China Medical University*

SBA-15 present a thicker and more condensed silica walls providing a stronger structure and thermal stability, the highly ordered hexagonal mesopores that is different to the micropores limit the channel size. The mesoporous materials could be more suit for the template of catalyst and mass transfer efficiency in chemical transfer procedures.

Therefore, the thermal stability, strong structure and chemical properties are the main reasons to select SBA-15 as the catalyst support. Transition metals such as Ni, Co, Fe, and Mo were selected as catalysts to conduct the chemical transformation. The specific surface area of original SBA-15 was about 680 m<sup>2</sup>/g and the catalysts impregnated abundances were from 2-8% corresponding to the specific surface area was 560-470m<sup>2</sup>/g for Fe-SBA-15, 440-340m<sup>2</sup>/g for Ni-SBA-15, and 410-340m<sup>2</sup>/g for Co-SBA-15. The increase of impregnated metal loadings corresponding to reduce the specific surface area and pore volume of templates. To understand the physicochemical properties of SBA-15 and metal loading templates, they were analyzed with nitrogen adsorption/desorption isotherms, and scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Resulted indicated the sequence of nitrogen adsorbed amount was SBA-15 > Fe-SBA-15

> Ni-SBA-15 > Co-SBA-15, under 5% metal loading. Some hexagonal pore structure in the SBA-15 and the structure was also determined for the metal loading SBA-15 in Figure 2.



ID-134

**Enhancing the corrosion resistance, platelet activation and antibacterial adhesion of biomedical titanium surface through formation of mixed nano-/sub-micron-scale TiO<sub>2</sub> network topography***H. Huang<sup>1</sup>, W. E. Yang, Z. H. Chen, Y. S. Sun<sup>2</sup>*<sup>1</sup> National Yang-Ming University<sup>2</sup> Department of Dentistry, National Yang-Ming University, Taipei, Taiwan

In this study, a rapid electrochemical anodization process, applying anodic current, was used to create a mixed nano-/submicron-scale network oxide layer on biomedical titanium (Ti) surface for dental implant applications. Surface characteristics, including crystal structure, morphology and thickness, of the anodized Ti surface were analyzed using thin film X-ray diffractometer, field emission scanning electron microscope and transmission electron microscope, respectively. The corrosion resistance in acidic artificial saliva (AS), platelet activation and anti-bacterial adhesion of the anodized Ti surface were evaluated. Results showed that a TiO<sub>2</sub> network, with a lateral pore size of approximately 40-150 nm, topography was rapidly created on the anodized Ti surface. As compared to the untreated Ti surface, the mixed nano-/submicron-scale TiO<sub>2</sub> network topography on anodized Ti surface significantly enhanced the platelet adhesion and the expression levels of P-selectin and platelet derived growth factor, but decreased the adhesion of oral bacteria (*Streptococcus mutans*). Additionally, the dense interfacial oxide layer between the surface anodized layer and Ti substrate further improved the corrosion resistance, i.e. decreased the corrosion rate and anodic passive current, in AS. Based on the current data, we would conclude that through a rapid electrochemical anodization treatment, a mixed nano-/submicron-scale TiO<sub>2</sub> network surface topography was created on Ti surface with a dense inner interfacial oxide layer. This unique topography significantly enhanced the platelet activation and anti-bacterial adhesion as well as the corrosion resistance of biomedical Ti surface for dental implant applications.

**Keywords:** Titanium; Nano-/submicron-scale network; Corrosion resistance; Platelet activation; Anti-bacterial adhesion.

ID-154

**Application of the Algerian diatomite in adsorption of diclofenac**

*O. Ghabeche<sup>1,2</sup>, S. Boukhezar<sup>1</sup>, M. Boulkra<sup>1</sup>, H. Meradi<sup>1</sup>, S. Benayeche<sup>1</sup>, H. Gueroui<sup>1</sup>, N. Touati<sup>1</sup>, K. Labiod<sup>1</sup>, F. Aouadja<sup>1</sup>*

<sup>1</sup> *Industrial Technologies Research Center (CRTI/URMA).*

<sup>2</sup> *LR3MI, Mechanical Engineering Dept., Faculty of Engineering, BadjiMokhtar University.*

*Industrial Technologies Research Center*

Mesoporous amorphous silica of non-toxic nature has interesting properties, in particular its relatively large surface area, pores with adjustable diameter and abundant Si-OH bonds. The functionalization of this silica transforms it into an ideal candidate for biological applications such as cell marking, gene transfection or as contrast agents in MRI and especially in drug delivery systems. In this study, we try to use a natural amorphous silica: Algerian diatomite, for encapsulation and carrier of Diclofenac (DS), in this order, diatomite must be purified; the choice of purification mode plays an important role in the organization and volume pore of the final product. We use hydrochloric acid HCl (1%, 10%, 20%) for oxide removal, and then we test the treated diatomite in the absorption of the DS.

**Keywords:** Diatomite, mesoporous, adsorption, diclofenac, drug carrier, encapsulation.

ID-238

**Preparation of CaO-based sorbent from coal fly ash cenospheres for calcium looping process**S. Scaccia<sup>1</sup>, G. Vanga<sup>1</sup>, D. Mirabile Gattia<sup>1</sup>, S. Stendardo<sup>1</sup><sup>1</sup> ENEA

Calcium looping (CaL) is a calcium-based sorbent new technology for be applied in various CO<sub>2</sub> capture processes. With the aim to synthesized an inexpensive high-stable and anti-sintering sorbent, an industrial waste product derived from coal-fired power plant, the so-called coal fly ash (CFA) cenospheres, was employed as an inert supporting material. The CaO-based sorbent from CFA cenospheres (mainly composed of mullite and SiO<sub>2</sub>) was prepared via citric method. The resulting sorbent contained CaO free and two crystalline phases, namely gehlenite (Ca<sub>2</sub>Al<sub>2</sub>Si<sub>2</sub>O<sub>9</sub>) and anorthite (CaAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>), indicating that under the given synthesis conditions cenospheres completely trasformed to calcium aluminum silicate compounds. An optimized mesopore size particle distribution was belonged to CaO/ gehlenite/anorthite sorbent. These results could reflected in a high CO<sub>2</sub> capture stability of the sorbent over multiple cycles of carbonation/calcination. The initial CO<sub>2</sub> capture capacity of the sorbent was 0.35g CO<sub>2</sub> g<sup>-1</sup> sorbent, which was about three times the value of pure CaO (0.11g CO<sub>2</sub> g<sup>-1</sup> CaO), and it was reduced to 0.25g CO<sub>2</sub> g<sup>-1</sup> sorbent after 20 cycles remaining then stable over 200th cycles. From the presented results it can be argued that CaL process could be scalable by the re-using a coal-fired plant waste-product.

ID-398

**Enhancing the bio-corrosion resistance and bone cell responses of titanium dental implant surface by coating a hybrid layer containing porous biphasic calcium phosphates (BCPs)/dense tantalum pentoxide ( $Ta_2O_5$ )***Y.S. Sun<sup>1</sup>, H. Huang<sup>2</sup>*<sup>1</sup> *Department of Dentistry, National Yang-Ming University, Taipei, Taiwan*<sup>2</sup> *National Yang-Ming University*

The purpose of this study was to enhance the bio-corrosion resistance and bone cell responses of bio-inert titanium dental implant surface by coating a hybrid layer containing porous biphasic calcium phosphates (BCPs)/dense tantalum pentoxide ( $Ta_2O_5$ ). A simple hydrolysis-condensation process was used to create a hybrid layer on titanium surface for potential dental implant applications. Surface characterizations, including topography, cross-sectional morphology, chemical composition, functional groups, and wettability, were analyzed systematically. The bio-corrosion resistance was evaluated using polarization curve measurements in artificial saliva with and without fluoride ions. The human bone marrow mesenchymal stem cell responses, including adhesion, proliferation, and mineralization, were investigated. Results showed that the inner dense  $Ta_2O_5$  sublayer in the hybrid layer provided an excellent resistance to bio-corrosion in artificial saliva, regardless of the presence of fluoride ions. The outer porous BCP sublayer had a hydrophilic surface and played a positive role in adsorbing protein (albumin), and thus enhancing the bone cell responses, particularly cell proliferation and mineralization. We conclude that the hybrid layer on bio-inert titanium surface enhances the bio-corrosion resistance in simulated oral environments as well as the bone cell growth. The proposed surface treatment has high potential in titanium dental implant applications.

ID-462

**Study on nanostructured  $\text{MgH}_2$  with Fe and its oxides for hydrogen storage applications***D. Mirabile Gattia<sup>1</sup>, M. Jangir<sup>2</sup>, I. P. Jain<sup>2</sup>*<sup>1</sup> ENEA - SSPT-PROMAS-MATPRO<sup>2</sup> Centre for Non-Conventional Energy Resources, University of Rajasthan

The possibility of coupling renewable energy sources to suitable storage systems could speed up the substitution of carbon-based not sustainable and pollutant energy production plants. In the next future main challenges will be represented by the realization of large energy storage infrastructures directly connected to the grid which allow to equalize energy production fluctuations of renewable energy plants and peaks of demands. One of the methods to store large quantities of energy could be represented by hydrogen storage being batteries competitive for small or medium applications. As storing hydrogen in the liquid form requires to consume 30% of the energy content respect to that stored and high pressure systems are also energy consuming and presents some safety problems, the solution is represented by storing hydrogen at the solid state [1]. Magnesium hydride is one of the most suitable candidates for this application due to completely reversible hydrogen storage reactions. Moreover magnesium is a widespread element on the earth. Some disadvantages are represented by the relatively high desorption temperature, 300°C, at 1 bar ( $H=-75 \text{ kJ/molH}_2$ ) and slow kinetics. For this reason two approaches are followed to reduce hydrogen paths and fasten kinetics: nanostructuring and doping the material. In this work the preparation of nanostructured magnesium hydride has been realized by mechanical milling under inert gas in presence of iron and its oxides. The ball to powder ratio is 10:1 and the powders have been milled for 10 hours. Fe is a suitable catalyst for hydrogen storage as it largely fasten kinetics respect to undoped material, but also because it is a widespread and cheap material. In the optic of realizing large facilities for hydrogen storage the critical issues represented by cost and ease of supply should be taken into consideration. The work reports also the preparation of pellets which could be directly be used inside tanks presenting less problems respect to powders during tank cycling [2]. The pellets have been prepared by an uniaxial press and the effects of long term cycling will be discussed. The materials have been investigated by Sievert type apparatus in the range 250-350°C and 1-10 bars, Differential Scanning Calorimetry (DSC), Scanning Electron Microscope (SEM) with EDS for microstructure and catalyst distribution and X-Ray Diffraction.

[1] Jain IP, IJHE 2009;34:7368

[2] Mirabile Gattia D et al., IJHE 2016;41:14455

ID-485

**Utilization of bioinspired nickel aluminates films for methanol electrochemical detection.**

*P. Zúñiga, S. V. Rodríguez, C. G. Solís, R. F. Ramírez, M. R. González*

*Universidad de Guanajuato*

The use of natural structures like templates in the synthesis of materials is a new trend called bio-inspiration, which is based on the duplication of existing designs in the nature to obtain products and technologies suitable for human development. In nature, some structures, perform important functions such as capture, conversion, transport and storage of energy. Some others respond to light or affinity to certain chemical molecules, which makes them good for detection devices [1,2]. The sensitivity of the compounds used in sensors depends on the microstructure [3], which can be modified by synthesis methods, reaction parameters, doping different elements, or the duplication of the nature morphological structures. In this work, nickel aluminates were synthesized using the Pechini method with natural templates: *Helianthus annuus* (sunflower), *Leucaena leucocephala* (white mimosa) and *Blattodea* (cockroach). The obtained materials were tested to be used in the electrochemical detection of methanol. Also, the materials were characterized with the X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and UV-VIS spectroscopy, furthermore. For the electrochemical tests, a conventional three electrodes electrochemical system was used: Ag/AgCl 3M as reference electrode, Pt wire as the counter electrode and a film made with the synthesized nickel aluminates deposited on FTO (fluorine doped tin oxide) as a working electrode. A solution of 0.5M Na<sub>2</sub>SO<sub>4</sub> sat pH 12 was used as support electrolyte. Using electrochemical techniques as Cyclic Voltammetry and Chronoamperometry, we obtained the conditions for the methanol electro-chemical detection of. The results show that the boundary values and detection range are promised, especially for nickel aluminates in which the *Helianthus annuus* (sunflower) template was used.

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## PLENARY LECTURE

Chair: L. Greer

**Heterogeneous dynamics of metallic glass-forming liquids**

P. Voyles

*Department of Materials Science and Engineering, University of Wisconsin, USA*

Metallic glasses are known for their outstanding mechanical strength but limited plasticity. Significant Glasses are complex materials. They exist in a variety of metastable states with different enthalpies, with a wide variety of local atomic arrangements, and those atoms rearrange at different rates in different places. Much of this complexity occurs at the nanoscale, including medium-range structural order and spatially heterogeneous dynamics in the supercooled liquid near  $T_g$ . Electron nanodiffraction is well-suited to probing this key length scale. Electron correlation microscopy (ECM) is the study of temporal fluctuations in nanodiffraction, are sensitive to structural rearrangements in the supercooled liquid [1]. The time-time autocorrelation function of the diffracted intensity can be fit to a stretched exponential,  $g_2(t) = 1 + A \exp[-2(t/\tau)^\beta]$  to obtain the structural relaxation time  $\tau$  and stretching exponent  $\beta$ , both with sub-nanometer spatially resolution. A four-point two-time, two-space correlation function can be fit to obtain a characteristic length  $\xi$  along with  $\tau$ . We have used ECM to study the dynamics in the supercooled liquid region of  $\text{Pt}_{57.5}\text{Cu}_{14.7}\text{Ni}_{5.3}\text{P}_{22.5}$  nanowires from  $T_g$  (507 K) to  $T_g + 16$  K (523 K). The data constitute the first spatially-resolved images of spatially heterogeneous dynamics in a supercooled liquid. The characteristic time scale  $\tau$  varies from  $>500$  seconds to a few seconds, and the characteristic length scale  $\xi$  varies from 1.4 to 0.8 nm with increasing temperature. The viscosity calculated from the mean relaxation time is in good agreement with bulk viscosity measurements.  $\xi(\tau)$  over this limited temperature range agrees with all of the major microscopic theories of the glass transition. The nanowires also exhibit a near-surface region with dynamics consistently an order of magnitude faster than the bulk. The thickness of the layer is  $\sim 0.7$  nm, which is too thick to arise from a surface monolayer. Instead, it is similar to the length scale of cooperatively rearranging regions in the liquid, so we speculate that the fast dynamics arise from trajectories of those regions that sample the free surface. The fast dynamics of the surface region may influence the surface-driven crystallization of the wires and may be related to the suppressed  $T_g$  observed in nanoconfined liquids.

[1] L. He, P. Zhang, M. F. Besser, M. J. Kramer, & P. M. Voyles, *Microsc. Microanal.* 21, 1026 (2015).

[2] P. Zhang, J. J. Maldonis, Z. Liu, J. Schroers, P. M. Voyles, *Nat. Commun.* 9, 1129 (2018).

Wednesday 4 July morning - 10:00/11:00

Parallel Session 1  
**METALLIC GLASSES VI**  
Chair: M. Atzmon



**ID-304 (Invited)****Athermal changes in structure induced by thermal cycling of metallic glasses**

L. Greer

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On heating metallic glasses, thermal activation can permit evolution of the glassy structure towards equilibrium in various ways: structural relaxation, glassy phase separation, crystallization. Below about 60% of the glass-transition temperature, however, such thermally activated structural changes are not expected — yet changes in the glassy structure, presumed to be largely athermal, do still occur, particularly in connection with changing the temperature of the glass, and explored through thermal cycling. That thermal cycling might achieve rejuvenation was first suggested by Ketov et al. [1], who pointed out that thermal strains in glasses must have a significant non-affine component, and that this component may induce structural change especially in metallic glasses. This overview considers what is known from a now-wider range of physical experiments, noting that: (i) in contrast to the presumption in Ref. [1], thermal cycling may induce relaxation as well as rejuvenation; (ii) some properties are strongly affected and not others. The atomistic structure of liquids is dependent on temperature: the characteristic haloes in the radial distribution function do not shift equally with temperature change, and nearest-neighbour distances can even appear to shorten on heating. In contrast, glassy states are conventionally taken to be isoconfigurational — yet recent diffraction evidence suggests otherwise, with structural changes as a function of temperature somewhat similar to those in the liquid state. Molecular-dynamics simulations will be used to explore the mechanisms of athermal structural changes induced by thermal cycling. The prospects for useful improvement of metallic-glass properties will be assessed.

[1] SV Ketov, YH Sun, S Nachum, Z Lu, A Checchi, AR Beraldin, HY Bai, WH Wang, DV Louzguine-Luzgin, MA Carpenter and AL Greer, Rejuvenation of metallic glasses by non-affine thermal strain, *Nature* 524 (2015) 200–203.

**ID-180****Statistics and the spatiotemporal correlations of stress and strain in model bulk metallic glasses.**

*A.E. Lagogianni, M. Hassani, F. Varnik*

*Interdisciplinary Centre for Advanced Materials Simulation (ICAMS), Ruhr-Universität Bochum, Bochum, Germany*

Spatiotemporal correlations and statistics of stress and strain in glass forming model systems are investigated both under steady shear and in the quiescent case. The study is performed via molecular dynamics simulations at various temperatures, ranging from the supercooled liquid regime down to the athermal limit. Long range correlations are observed both in the quiescent systems and under steady shear. Regarding the statistics of stress drops, it is shown that, independently of the deformation modes, avalanche dynamics obeys power law below and above yielding. In contrast to this, frequency, average magnitude of stress drops and the instantaneous shear modulus are distinct in the elastic and steady state (plastic) regimes.

ICAMS acknowledges funding from its industrial sponsors, the state of North-Rhine Westphalia and the European Commission in the framework of the European Regional Development Fund (ERDF).

A. E. Lagogianni and M. Hassani are supported by the German Research Foundation (DFG) under the project numbers VA205/16-1 and VA 205/18-1, respectively.

[1] Varnik F. et al, Phys. Rev. E 89, 040301(R) (2014)

[2] Hassani M. et al, JSTAT, (2016)

[3] Hassani M. et al., EPL 121, (2018)

[4] Liu C, et al., Phys. Rev. Lett.116, 065501 (2016)

[5] Dubey A.K. et al., Phys. Rev. Lett. 116, 085502, (2016)

ID-136

**Structure relaxation of a severely deformed Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> bulk metallic glass***A.H. Shahkhalil, H. Rösner, S. Divinskiy, W. Gerhard**Institute of Materials Physics University of Münster*

Relaxation behavior of a Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> bulk metallic glass as a result of severe plastic deformation via high-pressure torsion (HPT) and subsequent annealing treatments was analyzed. Amorphous samples were produced by copper mold casting in a melt spinner under argon atmosphere. X-ray diffraction, differential scanning calorimetry (DSC), and Transmission Electron Microscopy (TEM) measurements were performed. The degree of deformation was systematically varied by applying different numbers of rotation by HPT from 0 (just compression) to 10 turns. HPT causes significant changes of the thermo-mechanical properties of the Pd<sub>40</sub>Ni<sub>40</sub>P<sub>20</sub> bulk metallic glass. It turned out that unlike after plastic deformation by cold-rolling, room temperature HPT processing induced a distinct crystallization-like transformation in the deeply undercooled liquid above the glass transition which. The structural relaxation induced by annealing below the glass transition temperature shows a significant impact on the crystallization signals and created an endothermic signal that resembles a second glass transition which indicates in fact a liquid-liquid phase transformation in the undercooled liquid. The results are discussed in conjunction with the dedicated TEM investigations for annealed and as-deformed amorphous states.

Wednesday 4 July morning - 10:00/11:00

Parallel Session 2  
**NANOSTRUCTURED MATERIALS VI**  
Chair: L. Battezzati

**ID-116 (Invited)****Tri-segmented magnetic nanowires with antiparallel alignment: suitable platforms for biomedical applications with minimized agglomeration?**

*E. Pellicer<sup>1</sup>, J. Nogués<sup>2,3</sup>, J. Sort<sup>1,3</sup>, J. Zhang<sup>1</sup>, M.D. Baró<sup>1</sup>, S. Suriñach<sup>1</sup>*

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<sup>2</sup> *ICREA*

<sup>3</sup> *ICN2*

To expand the range of applications of conventional (i.e., “single-material”) magnetic nanowires (NWs), several segments comprising different magnetic materials can be incorporated in the NWs’ architecture, rendering additional functionalities. The resulting hybrid (i.e., segmented) NWs offer enhanced performance either due to the synergy between the properties of each building block, or due to interfacial effects arising from the interaction between the various magnetic materials comprised in the NWs.

In particular, tri-segmented NWs containing a soft (e.g., Ni) and a hard (e.g., PtCo) magnetic segment separated by a non-magnetic spacer (e.g., Cu), exhibit staircase-like hysteresis loops with tunable shape that depends on the relative length of the two magnetic segments, their coercivity, and the respective values of saturation magnetization. Interestingly, fully-compensated trisegmented NWs (with the soft and hard segments antiparallel to each other, like in a synthetic antiferromagnet) can be easily prepared by electrodeposition. Analytic calculations demonstrate that the interwire magnetic interaction from such NWs is reduced compared to single-component NWs with the same length or the tri-segmented NWs with the two ferromagnetic counterparts parallel to each other [1-3]. Hence, artificially-built antiferromagnetic NWs minimize the problem of magnetic agglomeration, which can eventually lead to thrombosis and other undesirable diseases.

[1] J. Zhang et al., ACS Appl. Mater. Interf. 8 (2016) 4109

[2] S. Agramunt-Puig et al., New J. Phys. 18 (2016) 013026

[3] J. Zhang et al., Appl. Mater. Interf. 3 (2016) 1600336

ID-191

## Novel and sensitive immunosensor based on metal-enhanced fluorescence by nanostructured surface: application to human IgG detection in urine

*B. Della Ventura*<sup>1</sup>, *M. Gelzo*<sup>2</sup>, *A. Dello Russo*<sup>2</sup>, *A. Morone*<sup>3</sup>, *B. Edmondo*<sup>4</sup>, *G. Castaldo*<sup>2</sup>, *G. Francesco*<sup>5</sup>, *R. Velotta*<sup>1</sup>

<sup>1</sup> *Università di Napoli "Federico II" - Dipartimento di Fisica*

<sup>2</sup> *Università di Napoli "Federico II" - Dipartimento di Biotecnologie e Medicina Molecolare*

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<sup>4</sup> *Università di Napoli "Federico II" - Centro Ricerche Biomateriali*

<sup>5</sup> *Università di Napoli "Federico II" - Dipartimento di Ingegneria Elettrica*

In recent years the development of novel interfaces for sensitive and specific biosensors is greatly increasing and the bio-inspired super-hydrophobic surfaces (SHSs) is an exciting example [1]. Recently, SHS has been combined to gold nanoparticles to achieve metal enhanced fluorescence effects [2], whereby the sensitivity can reach unprecedented levels. Here, we advance the current state of fluorescence-based sensing technology in medical diagnostics and biotechnology by functionalizing the SHS by PIT [Photochemical Immobilization Technique [3]] able to anchor antibodies upright to the surface. We applied this novel method to realize an immunosensor for the detection of Human IgGs in urine.

The resulting nanostructured chip is combined with a fluidic cell where all the relevant steps of the detection take place. The sandwich configuration so realized warrants high specificity with an impressive fluorescent signal even at very low Human IgG concentration in urine. The dose-response curves allow us to estimate a limit of detection (LOD) of only 150 picomolar with linear response up to 550 picomolar.

It is worth to highlight that given the principle of detection underlying our immunosensor, it is expected that such LODs are kept even with small molecules. The source of the background in our measurements is essentially due to environmental light collected by the microscope. In fact, by blocking the stray light reaching the detector and by increasing the exposure time up to 30 s, we have been able to reach femtomolar range thereby paving the way to a novel class of nanostructured biosensors for the diagnostics applications.

[1] E. Ueda and P. A. Levkin, *Adv Mater* 25, 1234–1247 (2013).

[2] F. De Angelis, F. Gentile, F. Mecarini, G. Das, M. Moretti, P. Candeloro, M. L. Coluccio, G. Cojoc, A. Accardo, C. Liberale, R. P. Zaccaria, G. Perozziello, L. Tirinato, A. Toma, G. Cuda, R. Cingolani and E. Di Fabrizio, *Nature Photonics* 5, 682–687 (2011).

[3] R. Funari, B. Della Ventura, C. Altucci, A. Offenhäusser, D. Mayer, R. Velotta, *Langmuir* 32, 8084–8091 (2016).

## ID-50

**Microstructure and surface design of metastable beta-Ti alloys for biomedical use**

*A. Gebert, S. Pitz, R. Schmidt, J. Freudenberger, M. Calin*

*IFW Dresden*

Beta-Ti alloys are the promising new generation of materials for load-bearing bone implant applications substituting currently used Ti and  $Ti_6Al_4V$ . Alloys of the metastable Ti-Nb system are particularly interesting as they exhibit in the cast, solution-annealed and quenched state very low Young's modulus values of ~60 GPa (40-45wt.-% Nb), which yield a comparatively low implant stiffness contributing to the reduction of stress shielding effects. However, for optimum mechanical biofunctionality the materials strength must be increased. Appropriate thermomechanical processing strategies including warm and cold rolling as well as annealing steps were developed. Grain refinement of the beta-phase, work hardening and precipitation of secondary phases, i.e. of alpha-phase or nanosized omega-phase, are demonstrated to be effective for significantly increasing yield and tensile strength and to control a low Young's modulus. Alternatively, powder metallurgical processing of Ti-Nb alloys was successfully applied. Hot compaction or spark plasma sintering of gas-atomized and intensively milled Ti-45Nb powder yielded fully dense samples with nanograin microstructure exhibiting very high compressive yield strength of >900 MPa and low Young's modulus ~70 GPa.

Ti-Nb alloys are composed of non-toxic elements and thus, are biocompatible. However, their naturally passivated surfaces are bioinert and do not enable optimum bone tissue growth. Chemical modification techniques were developed to change the morphology and the chemical nature of those alloy surfaces. Chemical etching in oxidative acid yields nanoroughness and triggers the passive layer growth. In *in vitro* studies, those alloy surfaces caused a better stimulation of bone-forming cell activity than those of cp-Ti. Enhanced surface oxidation is possible by electrochemical anodization. In F-containing solutions self-organized layers of oxide nanotubes grow with higher aspect ratios than those on cp-Ti. Plasma electrolytic oxidation yields a two-layer structure with a thick microporous outer oxide. For both techniques the oxide growth on the beta-alloy follows the principal mechanisms that are known for Ti. Nb species cause enhanced layer thickness growth, morphology changes and mixed oxides.

This work is funded by the DFG as part of SFB/Transregio 79.

Wednesday 4 July morning - 10:00/11:00

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY IV**  
Chair: J.S.C. Jangi



## ID-102

**High entropy alloys for hydrogen storage applications**

G. Zepon<sup>1</sup>, D. Leiva<sup>2</sup>, V. Aranda<sup>1</sup>, R.i Strozi<sup>1</sup>, T. Ishikawa<sup>1</sup>, W. Botta<sup>1</sup>

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<sup>2</sup> Department of Materials Engineering, Federal University of São Carlos, São Carlos, Brazil

Metal hydrides have been considered as the most promising solution for safe storage of hydrogen in the likely hydrogen-based energy system in the future. Despite the continuing advances in hydrogen absorption/desorption properties in conventional metal hydrides, such as  $MgH_2$ , TiFe and others, different approaches for processing, alloying, hydrides combinations to form composites, or even testing innovative types of alloys are still matter of strong research interest.

High entropy alloys are one of such innovative type of alloys. They are multi-component alloys, with five or more major elements, which typically stabilizes simple solid solutions. Recent reports demonstrated that high entropy alloys of particular systems can absorb much higher amounts of hydrogen than its constituents, reaching H/M ratio of 2.5, much superior than observed in conventional metal hydrides. In the present work, high entropy alloys of different systems, such as, MgZrTiFeCoNi, MgZrTiVFe, MgZrTiVFe, MgZrTiVFeCoNi and ZrTiVFeCoNi were produced and characterized in respect to hydrogen storage properties. The alloys were processed by high-energy ball milling under both argon and hydrogen atmospheres. Structural characterization was carried out by X ray diffraction (XRD) and scanning and transmission electron microscopy (SEM and TEM). H-absorption / desorption kinetics were measured in a Sievert's-type apparatus and by differential scanning calorimetry (DSC) coupled with thermogravimetric analysis (TGA) and mass spectrometry (QMS). Some of the studied alloys form a body-centered cubic (BCC) structure when milled under argon pressure. In the case of the  $MgZrTiFe_{0.5}Co_{0.5}Ni_{0.5}$  alloy the BCC phase is capable to absorb up to 1.2%wt. of hydrogen and during absorption it undergoes a phase transition forming a face centered cubic (FCC) high entropy hydride. This FCC hydride can be directly synthesized by high-energy ball milling under hydrogen pressure. These results are discussed in view of the possible mechanism associated with hydrogen absorption in high entropy alloys.

## ID-46

**Synthesis and hydrogen storage ability of the high-entropy alloys**

*V. Zadorozhnyy<sup>1</sup>, S. Klyamkin<sup>2</sup>, E. Berdonosova<sup>2</sup>, I. Tomilin<sup>1</sup>, A. Bazlov<sup>1</sup>, A. Abdulaev<sup>1</sup>, M. Zadorozhnyy<sup>1</sup>, M. Zheleznyi<sup>1</sup>, I. Shchetinin<sup>1</sup>, G. Milovzorov<sup>1</sup>*

<sup>1</sup> *National University of Science and Technology "MISiS"*

<sup>2</sup> *Department of Chemistry, Lomonosov Moscow State University*

The development of technically and economically efficient methods of storing and transporting hydrogen is an important issue of hydrogen energy technology. One of the most promising approaches to solving the problem is based on the ability of some intermetallic compounds and metals to react reversibly with hydrogen. Compared with other common hydrogen storage methods (compressed gas cylinders, cryogenic systems), metal hydride materials provide greater compactness and safety, as well as high hydrogen purity due to the exceptional selectivity with respect to hydrogen-containing gas mixtures. Along with already widely used intermetallic hydrogen storage systems, multicomponent (high entropy) alloys can significantly increase the hydrogen capacity.

High entropy alloys have been studied actively in recent times and they aroused great interest in the scientific community, primarily due to their distinguished physical and mechanical properties. A lot of questions related to the optimization of the chemical composition and the ratio of components are still open. Therefore, works devoted to multicomponent alloys having almost equiatomic composition are of great fundamental and applied interest.

In the present work, we report experimental results on synthesis and the hydrogen-storage performance of a series of multicomponent (highly entropy) alloys. The effect of mechanical alloying and activation through high energy ball milling on the formation of nonequilibrium high-defective multicomponent compounds, as well as on their interaction with hydrogen, have been also investigated.

This work was supported by the Ministry of Education and Science of the Russian Federation in the framework of the Program aimed to increase the competitiveness of the National University of Science and Technology "MISiS" (No. 3-2017-016). The work was also supported in part by Russian Science Foundation, project No. 17-73-20272

ID-167

**Efficient hydrogen evolution on Zn doped MoS<sub>2</sub> nanosheets***J.R. Vargas Garcia<sup>1</sup>, A.M. Robledo<sup>2</sup>, K.N. Ba<sup>1</sup>*<sup>1</sup> *Instituto Politecnico Nacional-Esiquie, Depto. Ing. Metalurgia Y Materiales*<sup>2</sup> *Instituto Politecnico Nacional-Esiquie, Depto. ing. Quimica*

MoS<sub>2</sub>-based nanostructured materials have received increasing interest as catalysts for hydrogen evolution reaction (HER) owing to their chemical stability, relatively low cost and high catalytic activity. In this study, we report the synthesis of Zn-doped MoS<sub>2</sub> nanosheets through a solvothermal method using SiO<sub>2</sub> nanospheres as removable templates. Successful doping of zinc atoms into the MoS<sub>2</sub> lattice was attained by controlling the amount of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O precursor. Removal of SiO<sub>2</sub> templates lead to a highly porous nanosheet structure. The HER on Zn-MoS<sub>2</sub> nanosheets reached a current density of 10mA/cm<sup>2</sup> at -200 mV (mV vs. RHE). Chronoamperometry measurements showed negligible decrease of current density after 4 h at -200 mV (mV vs. RHE).

ID-165

**Hydrogen evolution on nanotubular MoS<sub>2</sub>-PtS<sub>2</sub>/C composites***A. Verdejo-Palacios<sup>1</sup>, R. González-Huerta<sup>2</sup>, J. García<sup>1</sup>*<sup>1</sup> *Instituto Politécnico Nacional-Esiquie, Depto. Ing. En Metalurgia Y Materiales*<sup>2</sup> *Instituto Politécnico Nacional-Esiquie, Lab. Electroquímica Y Corrosión, UPALM*

Nanostructured MoS<sub>2</sub>-based composites are promising materials for hydrogen evolution reaction. In this study, we report the synthesis of nanotubular MoS<sub>2</sub>-PtS<sub>2</sub>/C by incorporating Mo and Pt atoms into the multiwalled structure of carbon nanotubes using a vapor-phase decomposition method and subsequent sulfurization process in CS<sub>2</sub> vapor atmosphere. The electrochemical performance of nanotubular MoS<sub>2</sub>-PtS<sub>2</sub>/C for HER (hydrogen evolution reaction) was investigated in a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at room temperature by cycling and linear voltammetries. The pristine carbon nanotubes were chemically and structurally modified by the incorporation of Mo, Pt and S atoms. The formation of MoS<sub>2</sub> and PtS<sub>2</sub> dichalcogenides preserving the one dimensional morphology was observed. Nanotubular MoS<sub>2</sub>-PtS<sub>2</sub>/C composites showed superior electrochemical performance for HER than conventional Pt/C cathodes.

Wednesday 4 July morning - 10:00/11:00

Parallel Session 4  
**MAGNETIC, TRANSPORT AND OPTICAL PROPERTIES  
FROM NANOSCALE TO BULK I**  
Chair: K.N. Trohidou

**ID-468 (Invited)****Simultaneous local heating/thermometry based on plasmonic mag-netochromic nanodomes**

Z. Li<sup>1</sup>, A. Lopez-Ortega<sup>2</sup>, A. Aranda-Ramos<sup>3</sup>, J.L. Tajada<sup>1</sup>, J. Sort<sup>4,3</sup>, C. Nogués<sup>3</sup>, P. Vavvasori<sup>2</sup>, J. Nogués<sup>4,1</sup>, B. Sepúlveda<sup>1</sup>

<sup>1</sup> Catalan Institute of Nanoscience and Nanotechnology (ICN2)

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Advanced nanobiomedical applications have been traditionally based on chemically synthesized inorganic nanoparticles. Here we present a novel type of structure especially suited for diverse biomedical uses: magnetoplasmonic nanodomes. The nanodomes are composed of a combined, magnetic and plasmonic, hemispherical shell deposited onto self-assembled 100 nm diameter polystyrene beads. Their morphology allows creating nanoparticles that merge strong optical and magnetic anisotropies with a nearly spherical shape. The variation of the materials (e.g., Co/Au or Fe/Au) and their thicknesses in the shell enables tuning both the optical and magnetic properties of the nanostructures. The very high plasmonic absorption of the nanodomes in the near-infrared is used for very efficient local optical heating, i.e., photo-hyperthermia for cancer treatment. Moreover, the nanodomes magnetic character allows to remotely manipulate them. In particular, they can be easily rotated in a liquid using small alternating magnetic fields. Due to their optic anisotropy, this rotation can easily tracked optically using their different absorption depending on the orientation (i.e., a magnetochromic effect). Since the rotation of the nanoparticles depends strongly on the viscosity of the medium, which in turn depends on the temperature, the optical tracking of the rotation can be used to accurately determine the local temperature around the nanodomes, i.e., nanothermometry. Such intense magnetochromic effect, together with the fast rotation speed of the nanodomes and their high heating efficiency, enable the simple and highly sensitive simultaneous plasmonic heating and temperature detection, even for low particle concentrations and in highly inhomogeneous media (e.g. tissues or physiological fluids). Thus, combining the nanodomes efficient photo-hyperthermia with their nanothermometry capabilities, allows in-situ tracking the efficiency of diverse photo-hyperthermia treatments. Moreover, the spherical shape and small size of the nanodomes confers them a low invasiveness and the capacity to rotate at high frequencies, which represents important advantages with respect to other possible nano-heater/thermometer approaches.

We thank the Spanish MINEO (MAT2016-77391-R) for its financial support

**ID-494 (Invited)****Enhanced Magneto-Electric Effect in M-type Hexaferrites by Co substitution into Trigonal Bi-pyramidal Sites**

*J. E. Beevers<sup>1</sup>, C. J. Love<sup>1</sup>, V. Lanzarot<sup>1</sup>, S. A. Cavill<sup>1,4</sup>, H. Izadkha<sup>2</sup>, C. Vittoria<sup>2</sup>, R. Fan<sup>3</sup>, G. van der Laan<sup>3</sup>, S. S. Dhesi<sup>3</sup>*

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The control of magnetism using applied electric fields offer the possibility of a new generation of ultra-low power, high density storage. In this respect, magnetoelectric (ME) multiferroic materials are intensely studied in order to understand how different symmetry breaking orders exist in the same material and how these orders can be coupled. Among the few room temperature single-phase ME multiferroics reported, hexaferrites show potential for device applications as they exhibit a low field ME effect at room temperature [1].

The magnetoelectric effect in M-type Ti-Co doped strontium hexaferrite has been studied using a combination of magnetometry and element specific soft X-ray spectroscopies. A large increase ( $> \times 30$ ) in the magnetoelectric coefficient is found when  $\text{Co}^{2+}$  enters the trigonal bi-pyramidal site. The 5-fold trigonal bi-pyramidal site has been shown to provide an unusual mechanism for electric polarization based on the displacement of magnetic transition metal (TM) ions [2]. For Co entering this site, density functional calculations demonstrate an off-centre displacement of the cation which may induce a large local electric dipole as well as providing an increased magnetostriction enhancing the magnetoelectric effect.

[1] Y. Kitagawa, Y. Hiraoka, T. Honda, T. Ishikura, H. Nakamura and T. Kimura. *Nature Materials* 9,797 (2010).

[2] S-P. Shen, Y-S. Chai, J-Z. Cong, P-J. Sun, J. Lu, L-Q. Yan, S-G. Wang and Y. Sun. *Phys. Rev. B* 90, 180404 (R) (2014)

Wednesday 4 July morning - 11:30/13:00

Parallel Session 1  
**METALLIC GLASSES VII**  
Chair: J. Eckert



**ID-257 (Invited)****Real time determination of visco-plastic strain in metallic glasses via x-ray scattering**

*Y. Sun<sup>1</sup>, A.F.T. Leong<sup>2</sup>, H. Sheng<sup>2</sup>, J-S Park<sup>3</sup>, T.C. Hufnagel<sup>2</sup>*

<sup>1</sup> *Institute of Physics, Chinese Academy of Science*

<sup>2</sup> *Dept. of Materials Science and Engineering, Johns Hopkins University*

<sup>3</sup> *Advanced Photon Source, Argonne National Laboratory*

Metallic glass can relax at room temperature even under elastic deformation. A phenomenon called stress relaxation is observed in many bulk metallic glasses (BMGs): The stress decreases when the sample displacement is maintained at a constant value. It is true that anelasticity and visco-plasticity develop during stress relaxation and their magnitudes can be measured from the stress-recovery of the unloaded specimen. But it is also true that we know little about when and how visco-plasticity happens during stress relaxation from this conventional method. Therefore, a real-time determination of the visco-plastic strain is needed.

Here we present a new solution via x-ray scattering. We performed four-point bending on cerium (Ce)- and zirconium (Zr)- based BMG plates and recorded their real-time x-ray diffraction patterns in situ. Although the specimens were held at a fixed deflection so that their macroscopic strain is constant, we found there are real-time position-shifts of the first diffraction peak in Ce-based metallic glasses. Moreover, after converting the position-shift into x-ray strain we found that the relative change in x-ray strain is smaller than the relative change of stress. By contrast, for Zr-based BMGs no obvious position shift of the x-ray peak during stress relaxation is observed.

The position-shift of the first diffraction peak in metallic glass reflects the change in atomic distances. It is then a question as to which mechanism affects these distances, anelastic or visco-plastic strain? Considering that  $T_g$  of Ce-based is smaller than the Zr-based BMG and hence viscous plastic flow is in favor of the former, we believe that the position-shift is attributed to the visco-plastic strain. Because the sample is under compression, a decrease of the compressive strain indicates a structural dilation. Therefore, our results demonstrate two things: first, the real-time visco-plastic strain is developing from the beginning of holding; and second, it induces dilation.

## ID-274

**On the processing, mechanical and structural characterization of ZrNi amorphous thin films**

M. Ghidelli<sup>1</sup>, M. Coulombier<sup>2</sup>, T. Pardoen<sup>2</sup>, H. Idrissi<sup>2</sup>, T. Schüll<sup>3</sup>, S. Gravier<sup>1,4</sup>, J.-J. Blandin<sup>1</sup>, R. Daudin<sup>1</sup>

<sup>1</sup> Univ. Grenoble Alpes, Grenoble INP / CNRS, France

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<sup>3</sup> The European Synchrotron Facility, ESRF, Grenoble, France

<sup>4</sup> VULKAM / Amorphous metallic micro-casting / France

The amorphous structure of metallic glasses is at the origin of their high mechanical properties. However, their use in everyday-life products is still limited by their low ductility at low temperatures. Moreover, because of the lack of crystalline long range order, i.e. grains, as well as grain boundaries, these materials are expected not to undergo modification of their mechanical behaviours with down-sizing. Their studies at small scales to understand the underlying deformation mechanisms has arisen more recently thanks to new experimental techniques and their potential applications in sectors where micro- and nano-parts are in demand.

The presentation focuses on the characterization at room temperature of the mechanical properties of self-actuated nanometer-sized ZrNi amorphous thin films processed by magnetron sputtering. These so-called “micro-machines” are produced throughout successive steps of materials depositions and optical lithography etching. This results in dog-bone shaped ZrNi specimens attached to a  $\text{Si}_3\text{N}_4$  layer containing high internal stresses. When this layer is selectively etched, the ZrNi films are released and deform in traction. The mechanical results show that an expected enhancement of the ductility is observed when the film thickness is decreased [1]. We show how the mapping of the spatial distribution of the local elastic strain can be investigated in such films using nano-beam synchrotron X-ray diffraction in transmission. Such cutting-edges technique sheds light on the local internal modifications of the atomic arrangement of the material under load. It will help us to wider our understanding of amorphous metallic alloys mechanical and structural properties at small scales.

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## ID-91

**Effect of cobalt addition on microstructural evolution, thermal stability and magnetic properties of Fe-based amorphous alloys**

*C.P. Velásquez, D.P. Cabarcas, F.J.B. Osorio*

*Universidad de Antioquia*

Due to their good soft magnetic properties, Fe-based amorphous alloys have been playing an important role in a wide number of industry applications, such as transformer cores, sensors, data storage devices, among others, not only for their performance, but because production costs, unlike their nanocrystalline counterparts, amorphous alloys barely need post-production treatments and, FeSiBP alloys are, in most cases, cheaper than those containing glass forming metals.

FeSiB alloys commercially used have been modified with different types of alloying elements in order to improve their performance; in one hand, the P, as an alloying element, contributes to improving the glass forming ability and thus reducing the dimensional limitation; on the other hand, Co tends to improve the thermal stability of the alloys by increasing the Curie temperature, allowing the alloys to retain their magnetic properties even at high working temperatures.

In the present study, 2mm wide and 30 $\mu$ m thick amorphous ribbons of the  $(\text{Fe}_{1-x}\text{Co}_x)_{77}\text{Si}_8\text{B}_{10}\text{P}_5$  systems were produced by melt spinning; the role of cobalt and its influence on the structure, thermal and magnetic performance was evaluated. X-ray diffraction (XRD) was used to confirm the structure of the as-cast samples and to analyze the structural evolution during devitrification as well as the analysis by transmission electron microscopy (TEM), saturation magnetization was analyzed by vibration sample magnetometry (VSM) and thermal stability was determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). We were able to obtain amorphous alloys through all the system; Curie temperature enhances up to 75% with Co addition, while saturation magnetization presents a slightly reduction; with cobalt addition, crystallization mode changes from one exothermic peak to two, the phases found in the system corresponds to  $\alpha$ -Fe,  $\text{Fe}_2\text{B}$  and  $\text{Fe}_3(\text{B,P})$  for the Co-free alloy and  $\alpha$ -Fe(Co),  $\text{Fe}_3(\text{B,P})$ ,  $\text{Co}_2\text{Si}$ ,  $\text{Co}_2\text{B}$ ,  $\text{Fe}_3\text{P}$ , FeB for the Co-containing alloys.

ID-206

## The effect of heat treatment on magnetic and thermal properties of finemet-type ribbons and microwires

*M. Churyukanova*<sup>1</sup>, *S. Kaloshkin*<sup>1</sup>, *E. Shuvaeva*<sup>1</sup>, *A. Aronin*<sup>2</sup>, *V. Zhukova*<sup>3</sup>, *A. Zhukov*<sup>3</sup>

<sup>1</sup> National University of Science and Technology "MISIS", Moscow, Russia

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<sup>3</sup> Dept. Phys. Mater., University of Basque Country, UPV/EHU San Sebastián 20018, Spain

Amorphous-nanocrystalline Finemet-type alloys are quite attractive due to their outstanding soft magnetic properties, combining high magnetization with rather high permeability. Such properties are acquired through the partial nano-crystallization of amorphous precursor.

We studied magnetic and thermal properties of Finemet-type alloys annealed at temperature below the crystallization temperature. The evolution of the Curie temperature,  $T_c$ , and the change of heat capacity in the vicinity of this magnetic transformation,  $\Delta C_p$ , were investigated using DSC. Relaxation of atomic structure of amorphous phase during the annealing was accompanied by increase of  $T_c$  and the disappearance of  $\Delta C_p$ . An increase of  $T_c$  is related to the relaxation of atomic structure of amorphous phase during annealing. Two relaxation processes with different mechanisms take place in amorphous state: topological ordering and chemical ordering. The XRD investigation showed that increase of the annealing temperature resulted in precipitation of -Fe(Si) nanocrystals. The fact that  $T_c$  data correlate with the structural alterations reflects the redistribution of the elements within amorphous precursor during the annealing. Precipitation of -Fe nanocrystalline nucleus in amorphous phase leads to the gradual degradation of  $T_c$  peak. The features of DSC data for the ribbon-shaped alloys and glass coated microwires were identified. The internal stress in microwires influences on the position and shape of the Curie peak on the DSC curve: raise of internal stresses value leads to shift of  $T_c$  and degradation of  $\Delta C_p$ . Decrease of the height of the  $T_c$  peak correlates with decreasing amount of the amorphous phase by crystallization, as well as with the magnetostriction decreasing of the remained amorphous phase. The shift of  $T_c$  peak allows to study kinetics of relaxation process and to estimate the apparent value of activation energy of relaxation process related to topological and chemical ordering: 29 and 87 kJ/mol for ribbon, 34 and 96 kJ/mol for microwire.

Considerable magnetic softening under nanocrystallization is observed in Finemet ribbons and microwires.

This study was supported by RFBR (Grant 16-53-48012)

ID-273

**Monte Carlo simulation of magnetic structures in amorphous alloys based on Rare-Earth metals***I. Pashueva, A. Bondarev, I. Bataronov**Voronezh State Technical University*

Using the Monte Carlo method in the frame of the Heisenberg model, the computer simulation of magnetic properties of Re-Tb and Re-Gd amorphous alloys was carried out. The temperature dependencies of spontaneous magnetization, Edwards–Anderson order parameter and magnetic susceptibility were calculated. The magnetic phase diagrams for the Re-Tb and Re-Gd amorphous alloys were constructed which were in a good agreement with the experimental results. The magnetization curves, hysteresis loops, remanent magnetization, coercive field, spin-spin correlation functions at different temperatures are also calculated. The magnetization relaxation after switching off the external magnetic field was also studied. Our results qualitatively agree with the experimental results obtained for amorphous alloys based on rare-earth metals.

Magnetic structure of Re-Tb and Re-Gd amorphous alloys was studied on the microscopic level with the use of spin-spin correlation functions and angle spin correlation functions. The difference between magnetic structures of the spin glasses with random anisotropy and with competition of exchange interactions was revealed.

Wednesday 4 July morning - 11:30/13:00

Parallel Session 2  
**NANOSTRUCTURED MATERIALS VII**  
Chair: T. Teranishi

ID-235

**CoFe<sub>2</sub>O<sub>4</sub>-ZrO<sub>2</sub> nanocomposites, modification with gold nanoparticles and their SERS application**

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One of the latest evolutions in the field of nanomaterials is represented by multi-functional nanosystems. Their characteristics make them suitable for various applications, such as devices for magnetooptical information processing, new catalysts and magnetically recoverable catalysts, fuel cells, nanomedicine [1] and also as efficient bio/nanosensors [2]. To obtain a suitable material for biomedical applications, as biosensor or complex drug delivery system, we design a system exploiting different properties in only one nanotools. The system is obtained loading, by wet impregnation method, the pores of mesoporous zirconia nanoparticles [3] with CoFe<sub>2</sub>O<sub>4</sub> [4] and trying to preserve the porosity and the possibility of surface modifications to achieve a complex drug delivery system. Moreover, gold nanoparticles, produced by laser ablation [5,6], are linked to the nanocomposite, using the affinity with sulfur groups, and modified with a SERS probe. In this way, a magneto-plasmonic nanosensor is made, is characterized with magnetophoresis and SERS is proved. The system is characterized in detail using different techniques, like electron microscopy and SQUID magnetometry.

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[2] Rashid, Z.; Soleimani, M.; Ghahremanzadeh, R.; Vossoughi, M.; Esmaeili, E.; Appl Surf Sci 2017, 426, 1023.

[3] Sponchia, G.; Ambrosi, E.; Rizzolio, F.; Hadla, M.; Del Tedesco, A.; Russo Spena, C.; Toffoli, G.; Riello, P.; Benedetti, A.; J Mater Chem B 2015, 3, 7300.

[4] Parma, A.; Freris, I.; Riello, P.; Cristofori, D.; de Julian Fernandez, C.; Amendola, V.; Meneghetti, M.; Benedetti, A.; J Mater Chem 2012, 22, 19276.

[5] Amendola, V.; Meneghetti, M.; J Mater Chem 2007, 17, 4705.

[6] Meneghetti, M.; Scarsi, A.; Litti, L.; Marcolongo, G.; Amendola, V.; Gobbo, M.; Di Chio, M.; Boscaini, A.; Fracasso, G.; Colombatti, M.; Small 2012, 8, 3733.

ID-211

**Detection of toxic/flammable gases by  $Mn_3O_4$  based sensors for safety, health and public security applications**

*L. Bigiani<sup>1</sup>, C. Maccato<sup>2</sup>, G. Carraro<sup>2</sup>, A. Gasparotto<sup>2</sup>, C. Sada<sup>3</sup>, E. Comini, D. Barreca<sup>4</sup>*

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<sup>4</sup> *CNR-ICMATE and INSTM, Department of Chemical Sciences, Padova University, 35131 Padova, Italy*

The efficient detection of toxic/flammable chemical compounds is a main challenge for safety, health and public security applications [1]. In this context, the development of new sensors that matching the “3 S” requirements (sensitivity, selectivity, stability) is of crucial importance for eventual practical applications. To this aim, metal oxide semiconductor nanomaterials, and in particular the p-type ones, has attracted a great attention towards the fabrication of gas sensors thanks to their appreciable catalytic activities in various oxidation reactions.

In this work, p-type  $Mn_3O_4$  nanosystems were grown by means of chemical vapor deposition (CVD) experiments on polycrystalline alumina substrates starting from the molecular precursor  $Mn(hfa)_2 \cdot TMEDA$  ( $hfa = 1,1,1,5,5,5$ -hexafluoro-2,4-pentanedionate;  $TMEDA = N,N,N',N'$ -tetramethylethylenediamine).

A detailed characterization of the obtained nanosystems was performed in order to have an insight into the influence of their chemico-physical properties as a function of two process parameters: reaction atmosphere (dry  $O_2$  vs.  $O_2 + H_2O$ ) and deposition temperature.

To evaluate the gas sensing performances, the obtained nanomaterials were integrated into solid state gas sensor devices and tested in the detection of selected analytes: ethanol, acetone as well as simulants of cyanide compounds (acetonitrile), and chemical nerve warfare agents (dimethyl methylphosphonate, DMMP).

The obtained results revealed attractive responses in particular for ethanol and acetone which were the highest ever reported in the literature for manganese oxide-based gas sensors [2]. In addition, the responses obtained at moderate working temperatures and low analyte concentrations for acetonitrile and DMMP were among the best reported up to date [1]. These evidences demonstrate that CVD preparation routes represent an effective way to gain a fine tuning of both chemico-physical properties and corresponding sensing performances of the prepared  $Mn_3O_4$  nanomaterials as a function of the adopted processing parameters.

[1] L. Bigiani et al., Towards the detection of poisonous chemicals and warfare agents by functional  $Mn_3O_4$  nanosystems, Submitted.

[2] L. Bigiani et al., Vapor phase fabrication of  $Mn_3O_4$  nanosystems: from synthesis to gas sensing applications, Submitted.



ID-456

**Magnetic nano-composites for biomedical and magnetocaloric application***A. Zelenakova, P. Hrubovcak<sup>1</sup>, O. Kapusta<sup>2</sup>, J. Kovac<sup>3</sup>, V. Zelenak<sup>4</sup>*<sup>1</sup> Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,<sup>2</sup> University of P.J. Safarik<sup>3</sup> Institute of Physics, Slovak Academy of Sciences<sup>4</sup> Department of Inorganic Chemistry, University of P.J. Safarik

The fabrication of nanocomposites containing metal/metal oxide nanoparticles loaded in mesoporous silica supports have received a considerable attention within the last years due to their high application potential in different fields such as development of magnetic sensors, efficient catalytic materials, energy applications and in biomedicine as contrast agents for magnetic resonance imaging, carriers in drug or gene delivery systems, or materials for hyperthermal treatment of tumors. Recently, there has been increasing interest in utilization of mesoporous silica as drug support for prolonged and better controlled drug administration. The physical properties of nanoparticles can be significantly affected by competing interactions between nanoparticles. Weak interparticle magnetic interactions lead to the superparamagnetic (SPM) behavior. In contrast, strongly interacting and dense NPs systems show spin glass (SG) behavior, and in analogy with atomic spin glasses are referred to as superspin glasses (SSG). Therefore a deep understanding of interparticle interactions between magnetic nanoparticles is crucial for their subsequent practical applications.

We have investigated the magnetic nanocomposites consisting of iron oxide (hematite,  $\text{-Fe}_2\text{O}_3$ ) and gadolinium oxide ( $\text{Gd}_2\text{O}_3$ ) nanoparticles loaded into the pores of the periodically ordered nanoporous silica with hexagonal (2D) or cubic (3D) symmetry. The structural characterization of the samples was carried out by  $\text{N}_2$  adsorption/desorption, HRTEM measurements, TG/DTA and using synchrotron related techniques such as Small-angle X-ray scattering (SAXS) and High-energy X-ray diffraction (HE-XRD) and by a SANS technique. The magnetic properties of the nanocomposites were investigated by the SQUID magnetometry. It was shown, that in spite of its non-magnetic nature the silica matrix significantly influences the magnetism of the samples. The magnetic properties are strongly affected by the strength of inter-particle interactions and dimensionality of the porous matrix. Such materials combine the advantages of mesoporous silica with 2D and 3D pore network as drug support and magnetic iron/gadolinium oxide nanoparticles as vectors allowing the pointed transfer the drug into the affected body organs with the assistance of external magnetic field and a large magnetic entropy change and a high refrigeration capacity at low temperatures enable to extend the application of studied material to cryomagnetic refrigeration.

## ID-404

**Using core-level shifts as a descriptor for identification of nanoparticles with optimized catalytic activity**

A.A. Tal<sup>1</sup>, W. Olovsson<sup>1</sup>, A. Posada-Borbon<sup>2</sup>, H. Grönbeck<sup>2</sup>, I.A. Abrikosov<sup>1</sup>

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<sup>2</sup> Chalmers University of Technology, Sweden

XPS techniques are efficient tools for nanoclusters characterization. However, fundamental understanding of the spectral features of the nanoclusters and their relation to the particles structure is still incomplete. We investigate the shifts of the core-level binding energies, the core-level shifts (CLS) in small gold nanoclusters using density functional theory calculations. The shift of the 4f -states is calculated for magic number nanoclusters in a wide range of sizes and morphologies. We find a non-monotonous behavior of the CLS with increasing size of the nanoclusters. We demonstrate that there are three main contributions to the Au 4f shifts: they depend sensitively on the interatomic distances, coordination numbers and quantum confinement effects. We explain the observation by the change of the on-site electrostatic potential [1].

Further, we investigate the correlation between the CLS and catalytic activity of nanoparticles. We study Pd nanocluster with icosahedral and octahedral morphology. The absorption of ethylene and the CLS at different sites of the nanoclusters was calculated from first principles. We show that there is significant correlation between them. Thus, we propose that XPS spectra may provide means for characterization of nanoclusters catalytic properties, and the CLS can be used as a descriptor for identification of nanoparticles with optimized catalytic activity.

[1] A. A. Tal, W. Olovsson, and I. A. Abrikosov, Phys. Rev. B 95, 245402 (2017).

## ID-83

**Nano-sized silicate hydrate for high strength and durable concrete**

*G. Ferrari<sup>1</sup>, G. Artioli<sup>2</sup>, M. Dalconi<sup>2</sup>, L. Valentini<sup>2</sup>*

<sup>1</sup> Mapei Spa

<sup>2</sup> Department of Geoscience, University of Padua

This paper describes a new additive capable to effectively promote the development of early high strength and to reduce the water permeability of cementitious materials. Early high strength development is important in concrete technology to speed up the concrete production both in cold climates and in precast industry. The reduction of the permeability to water prevents the introduction of aggressive salts in the capillary pores of the cement paste and, therefore, increases the durability of concrete structures. The new admixture is an aqueous suspension of nanosized metal transition polymeric silicate hydrate that catalyzes the homogeneous nucleation of calcium Silicate Hydrate (CSH) in the capillary pores of hydrating cement paste, promoting the early strength development. Furthermore, the crystallization of CSH in the capillary pores refines the capillary porosity of cement paste and significantly increases the resistance to water penetration under pressure. The mechanism of homogeneous crystallization of CSH was demonstrated by Synchrotron XRD microTomography (XRD- $\mu$ T) and by Scanning Electron Microscope (SEM) investigations. The effectiveness of the new admixture was demonstrated by mechanical tests on concrete specimens and by measuring the water permeability according to European Standard EN 12390-8. The new admixture increases the early strength development of concrete and can be used to produce concrete with outstanding mechanical performances and durability and it is highly effective in reducing the penetration of water, compared to other permeability reducing admixture admixtures, working with different mechanisms.

ID-148

**Towards micro- and nanostructured AlZnCu alloys cast from commercial-purity metals**

*W.K. Krajewski<sup>1</sup>, P.K. Krajewski<sup>1</sup>, A.L. Greer<sup>2</sup>, M. Faryna<sup>3</sup>, L. Rogal<sup>3</sup>*

<sup>1</sup> AGH University of Science and Technology, Faculty of Foundry Engineering

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<sup>3</sup> Institute of Metallurgy and Materials, Polish Academy of Sciences

Aluminium-based cast alloys are widely used due to their comparatively light weight and good strength. Within this group are AlZn-based alloys which have also good damping and tribological properties [1–2]. Unfortunately, sand castings of these alloys show a coarse dendritic structure which detrimentally influences plastic properties, e.g. elongation. That is why grain refinement of the so-called high-zinc aluminium alloys should be performed, e.g. by adding AlTi-based or Zn-Ti-based grain-refiners [2]. By inoculation with such additions, the grain size of an Al-20 wt.% alloy could be reduced from about 2000 microns to 100–150 microns [2]. In this work, we applied rapid cooling and inoculation, together or separately. Ternary Al-30 wt.% Zn-3 wt.% Cu (Al-30Zn-3Cu) and Al-30 wt.% Zn-20 wt.% Cu (Al-30Zn-20Cu) alloys were melted from commercial-purity Al and Cu (99.5%) and high purity Zn (99.99%). The melts were cast into sand and steel moulds with cylindrical cavities of, respectively, 12 mm and 3 mm diameter. For the Al-30Zn-20Cu alloy cast into the steel mould we obtained a significantly refined structure with grain size reduced to 5–10 microns.

This work was financially supported by the NCN National Science Centre – Poland under grant UMO-2015/18/M/ST8/00038. We will present changes of structure and properties of multicomponent high-zinc aluminium alloys cast into a copper mould without addition of the grain-refining master alloys and after inoculating the melt before pouring with 50–100 ppm Ti introduced with the above- mentioned refiners. The mechanisms underlying the observed microstructural changes will also be discussed.

[1] W.K. Krajewski, J. Buras, P.K. Krajewski, A.L. Greer, K. Faerber and P. Schumacher, *Materials Today: Proceedings* 2 (2015) 4978–4983.

[2] W.K. Krajewski, J. Buras, P.K. Krajewski, A.L. Greer, P. Schumacher, K. Haberl, *IOP Physics Conference Series: Materials Science and Engineering* 143 (2016) 012029.

Wednesday 4 July morning - 11:30/13:00

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY V**  
Chair: S. Nakamae

**ID-407 (Invited)****Nanofluids in energy systems- prospects and challenges***S.M.S. Murshed**University of Lisbon*

Nanofluids are suspensions of nano-sized (typically 1-100 nm) particles in conventional fluids[1]. This is one of the popular research fields that is receiving enormous interest from researchers around the globe. Although nanofluids were found to exhibit enhanced thermal and transport properties such as thermal conductivity, convective heat transfer coefficient and boiling critical heat flux, very limited research efforts have been made on their application in energy conversion and storage systems. In addition, most of the studies dealt with nanofluids use in solar energy systems such as different solar collectors, photovoltaic/thermal systems, solar water heaters, and solar power plant. Preliminary results demonstrated that nanofluids can boost the performances of those solar energy systems. For instance, nanofluids showed increase the electricity generation performance of solar power plant and enhanced the efficiency of solar collectors. On the other hand, nanofluids can save thermal energy and related cost through their superior cooling performances in various thermal management systems, which are the most widely used areas of nanofluids. However, there are challenges of applying nanofluids in those systems. One of such challenges is the long-term stability of these nanoparticles dispersed liquids [1]. Nevertheless, nanofluids are believed to play a big role in the future energy economy.

This presentation comprises of three parts. In the first part, application of conventional nanofluids in energy areas will be discussed and their performance particularly in solar energy systems will carefully be reviewed and analyzed. Potentials of new nanofluids and nanoparticles-based systems such as ionanofluids and nano-moltsalts in solar energy applications and storage will also be addressed. Second part of the presentation will focus on the prospect of these new nanoparticles- based liquids in sustainable energy applications and economic impact. Current and future challenges of these new fluids will be identified and some recommendations will be made to overcome those challenges and barriers in. Finally the talk will end highlighting the activities of the first European COST action network on nanofluids (Nanouptake), which is also dealing with the solar energy based nanofluids in addition to other areas of nanofluids.

[1] S.M.S. Murshed and C.A. Nieto de Castro, Nanofluids: Synthesis, Properties and Applications, New York: Nova Science Publishers. 2014.

ID-288

**Thermophoretic properties of colloidal dispersions of maghemite nanoparticles in ionic liquids based on TFSI anions.***M. Sarkar<sup>1</sup>, J. Riedl<sup>1</sup>, G. Mériquet<sup>1</sup>, G. Demouchy<sup>2</sup>, E. Dubois<sup>1</sup>, V. Peyre<sup>1</sup>, R. Perzynski<sup>1</sup>*<sup>1</sup> Sorbonne Université/ CNRS UMR 8234 – lab. PHENIX, Paris, France<sup>2</sup> Université Cergy-Pontoise, Département de la Physique, 33 Bd du Port, Cergy-Pontoise, France

Ionic liquids (ILs) are a wide class of solvents, purely constituted of ions, which can be liquid at room temperature and strongly differ from classical molecular solvents. They are used in many applications, mainly as green solvents to replace dangerous organic solvents, for example in thermoelectric applications [1].

Our work is aimed at developing new thermoelectric materials based on ionic ferrofluids, namely colloidal dispersions of magnetic nanoparticles in ionic liquids that are versatile, cost-effective and non-toxic to assist the economically and environmentally sustainable energy transition. For this purpose various types of ILs based on imidazolium, pyrrolidinium and ammonium cations with bis(trifluoromethane) sulfonimide (TFSI) anion and maghemite nano-particles have been synthesized and tested for stability. The structure of the colloidal suspensions is investigated by Small Angle Scattering (SANS/SAXS) measurements.

Thermoelectric applications require a precise determination of the various transport coefficients of the nanoparticles under a thermal gradient, namely Ludwig-Soret (thermophoretic) and Seebeck (thermoelectric) effects which are interlinked in such ionic systems [2]. Thermodiffusive and thermophoretic properties are studied here by Forced Rayleigh Scattering (FRS) [3]. A 1D sinusoidal grating with spatial periodicity ( $\Lambda$ ) is imaged in the volume of the liquid which causes a regular modulation of temperature ( $\Delta T$ ), due to the light-absorbing NPs. Ludwig-Soret effect then induces locally a regular array of NP's volume fraction in the dispersion. Owing to the determination of the local modulations of temperature ( $\Delta T$ ) and volume fraction ( $\Delta \phi$ ), we measure the Ludwig-Soret coefficient ( $ST$ ) in stationary conditions. The relaxation of the  $\phi$ -array at  $\Delta T = 0$  leads to the determination of the diffusion coefficient of the particles ( $D_m$ ). From the Ludwig-Soret coefficient it is also possible to determine the Seebeck contribution of the ionic ferrofluids.

We acknowledge funding from European project Horizon 2020 FET-PROACTIVE project, MAGENTA, associated with the Grant n° 731976.

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[3] Mériquet, G.; Demouchy, G.; Dubois, E.; et al., J. Non-Equilib. Thermodyn., 32, pp. 271-9, 2007.

ID-477

**Study of the Seebeck coefficient in a system of electrolyte with magnetic nanoparticles***M. Vasilakaki<sup>1</sup>, J. Chikina<sup>2</sup>, K. Trohidou<sup>1</sup>, A. Varlamov<sup>3</sup>*<sup>1</sup> *Institute of Nanoscience and Nanotechnology, NCSR "Demokritos"*<sup>2</sup> *IRAMIS, LIONS, UMR NIMBE 3299 CEA-CNRS, CEA-Saclay*<sup>3</sup> *CNR-SPIN*

Currently, liquid thermocells are receiving increasing attention as an inexpensive alternative to conventional solid-state thermoelectrics for low-grade waste heat recovery applications. The Seebeck coefficient of liquid thermoelectric materials has been demonstrated to be increased by using charged colloidal suspensions namely ionically stabilized magnetic nanoparticles dispersed in electrolytes.

[1] It is expected that the resulting enhanced Seebeck effect comes from the contribution of both the electrolytes and the charged magnetic nanoparticles.

We study for the first time the role of the magnetic nanoparticles in the formation of the giant thermoelectric signal based on a thermodynamic approach and Kelvin formula [2-3]. An analytic expression for the chemical potential of electrolytes with magnetic nanoparticles taking into account their dipole-dipole interactions has been developed.

Monte Carlo simulations of an assembly magnetic nanoparticles interacting via dipolar interactions [4] have been performed, to calculate the temperature, particle size and concentration dependence of the chemical potential. Our calculations demonstrate the important contribution of the dipolar interaction in the enhancement of the Seebeck coefficient and the role of the magnetic particle characteristics.

This work supported by the H2020-FETPROACT-2016-2017, Project MAGENTA (GA No 731976)

[1] T. J. Salez, B. Huang, M. Rietjens, M. Bonetti, C. Wiertel-Gasquet, M. Roger, C. L. Filomeno, E. Dubois, R. Perzynski, and S. Nakamae, accepted in *Phys. Chem. Chem. Phys.* (2017)

[2] M. R. Peterson and B. S. Shastry, *Phys. Rev.*, B82,195105 (2010).

[3] A.A.Abrikosov, *Fundamentals of the theory of metals*, Elsevier, 1988.

[4] M. Vasilakaki, G. Margaris and K. Trohidou, "Monte Carlo simulations on the magnetic behaviour of nanoparticle assemblies: Interparticle interaction effects", *Nanoparticles Featuring Electromagnetic Properties: From Science to Engineering*, 2012: 105-131, Editors: Alessandro Chiolerio and Paolo Allia



ID-493

**Charge distribution on the surface of  $\text{CoFe}_2\text{O}_4$  nanoparticles***N. Ntalli<sup>1</sup>, K. N. Trohidou<sup>1</sup>, D. Peddis<sup>2</sup>*<sup>1</sup>*Institute of Nanoscience and Nanotechnology, NCSR 'DEMOKRITOS', Athens, Greece*<sup>2</sup>*Istituto di Struttura della Materia-CNR, Monterotondo Scalo, Roma, Italy*

Charged surfaces of nanoparticles have very important contribution in the ionic liquids based ferrofluids for energy applications [1]. The charge distribution on the particles surface plays significant role on their stability inside the liquid.

We perform DFT calculations using the VASP package [2, 3] to study the charge distribution in Co ferrite nanoparticles. The ionic distributions used are the inverse spinel one for the uncoated  $\text{CoFe}_2\text{O}_4$  and two partial spinel structures obtained experimentally for particles coated with a) diethylene glycol (DEG) and b) Oleic acid [4]. The calculation of the electric field for the charge distributions obtained indicates that the coated particles show a slower reduction of the electric field with the distance. This effect is more pronounced in the glycol coated particles. For these nanoparticles, we expect that the coated will improve their colloidal stability compared with the uncoated and the oleic acid coated ones.

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Wednesday 4 July morning - 11:30/13:00

Parallel Session 4  
**MAGNETIC, TRANSPORT AND OPTICAL PROPERTIES  
FROM NANOSCALE TO BULK II**  
Chair: A. Zhukov

**ID-391 (Invited)****Out-of-equilibrium cation distribution in ferrites: static and dynamic magnetic properties**

*G. Barrera<sup>1</sup>, M. Coisson<sup>1</sup>, F. Celegato<sup>1</sup>, S. Raghuvanshi<sup>2</sup>, S.N. Kane<sup>2</sup>, P. Tiberto<sup>1</sup>*

<sup>1</sup> INRiM

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Ceramic spinel ferrite particles exhibit different, peculiar physical properties such as high electrical resistivity, low-power loss at high frequency, high magnetic saturation and coercivity. These features make them a viable alternative for several applications, i.e. as to replace partially rare-earth elements in permanent magnets as well as suitable materials for devices operating at high frequency. In particular, the thermal stability of the non-equilibrium cation distribution and the filling of empty interstitial sites in the spinel ferrites structure with suitable cations allow to finely tune the ferro-magnetic behavior of ferrites according to practical demands. In this talk, Zn-ferrite powders with Co and Li substitution ( $\text{Co}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$  ( $0.08 \leq x \leq 0.56$ ) and  $\text{Li}_{0.5-x/2}\text{Zn}_x\text{Fe}_{2.5-x/2}\text{O}_4$  ( $0.0 \leq x \leq 1.0$ )) prepared by a sol gel auto-combustion method have been investigated through the combined use of structural and dc/ac-magnetization measurements. EDS spectra are performed to evaluate the samples chemical composition, whereas the X-ray diffraction measurements allow to determine the non-equilibrium cationic distribution as well as the lattice parameter and the oxygen position as function of Zn content. Dc/ac-magnetic characterizations were performed with the aim to improve the knowledge about the interplay between the structural properties and magnetic behavior. In particular, cation distribution in the lattice resulted to have a strong influence on the overall magnetization process. To this aim, the hysteresis loops under static and alternating magnetic field (frequency of 69 kHz) at selected vertex field values have been measured in order to evaluate the energy losses. This allows to identify the prospective exploitation of ferrites to operate in different field conditions taking advantages of the fine tuning of cation distribution.

ID-212

**Dynamical magnetic properties of interacting ultra-small nanoparticle systems**

R. Mathieu<sup>1</sup>, M.H. Waltin<sup>2</sup>, P. Nordblad<sup>1</sup>, M. Vasilakaki<sup>3</sup>, G. Margaris<sup>3</sup>, K.N. Trohidou<sup>3</sup>, N. Yaacoub<sup>4</sup>, M. Belluscì<sup>5</sup>, F. Padella<sup>5</sup>, D. Fiorani<sup>6,7</sup>, D. Peddl<sup>6</sup>

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<sup>7</sup> Center of Nanomaterials Research, Immanuel Kant Baltic Federal University, Kaliningrad, Russia

The magnetic interaction between nanoparticles brings forth collective states such as superspin glass states. The dynamical magnetic properties of superspin glasses are qualitatively similar to those of atomic spin glasses [1]. That includes a (super)spin glass phase transition, and dynamical features such as aging, memory, and rejuvenation phenomena [2]. However, the superspin glass states are formed by magnetically interacting superspins, much bigger than atomic spins. We have here investigated the superspin glass state ( $T_g \sim 46$  K) of a dense assembly of 2 nm  $\text{MnFe}_2\text{O}_4$  nanoparticles by magnetometry, recording the zero-field-cooled (ZFC), thermo- and isothermal remanent (TRM and IRM) magnetization after specific protocols [2]. We find that, in spite of the significant disorder affecting inter- and intraparticle interactions, the glassy state displays the same dynamical features and superposition as atomic spin glasses. Monte Carlo simulations considering a mesoscopic model of the nanoparticle system [3] reproduce well the experimental findings. The effect of the superspin dimensionality is discussed [4].

The Swedish Research council (VR) and the Wenner-Gren Foundations are thanked for financial support.

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ID-229

**On the magnetic properties of Fe-doped hydroxyapatite nanoparticles***A. Adamiano, A. Tampieri, M. Iafisco, M. Sandri, S. Sprio*

CNR - ISTEC

Magnetic nanoparticles (MNPs) have strongly emerged in nanomedicine since their successful application in magnetic drug delivery, hyperthermia and contrast agent for diagnostic imaging. MNPs are required to be targeted to a particular tissue/organ in order to maximally accomplish their function, leading to high concentrations in a localized area and thus to the possible arising of toxic implications. To circumvent these issues, numerous studies were focused on doping well-known biocompatible materials with magnetic ions to obtain intrinsically safe and biocompatible magnetic biomaterials. At this regard, the control over the doping mechanism is a key factor for an accurate synthesis of the targeted biomaterial with high biological and magnetic properties.

In this work, we investigate the relation between the synthesis temperature and the structural and magnetic properties of hydroxyapatite nanophases synthesized by wet neutralization method in the presence of  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ions. In particular, we demonstrate how the control of the synthesis parameters uniquely yields the formation of hydroxyapatite nanophase exhibiting partial calcium substitution with both iron ions - and the simultaneous formation of iron oxide-based secondary phase - thus obtaining a nanocomposite (FeHA) whose structural and magnetic properties are strictly related to the doping temperature determining the final iron setting.

## ID-44

**Curie temperature changes in Nd doped YIG by mechanosynthesis**

*E.B. López<sup>1</sup>, F.S. de Jesús<sup>1</sup>, A.M.B. Miró<sup>1</sup>, C.A.C. Escobedo<sup>2</sup>*

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The effect of substitution of  $Y^{3+}$  by  $Nd^{3+}$  on the structural and magnetic properties of neodymium doped yttrium iron garnet,  $Nd_xY_{3-x}Fe_5O_{12}$  ( $Nd_xYIG$ ) varying  $x$  from 0 to 2.5 is presented. Oxide powders were mixed in a stoichiometric ratio, milled for 5 h using high-energy ball milling and sintered at  $1100^\circ\text{C}$  for 2 h to obtain  $Nd_xYIG$ . It is found in all compositions that mechanical milling followed by an annealing treatment at low temperature ( $1100^\circ\text{C}$ ) promotes the complete structural transformation. The X-ray diffraction patterns confirm the complete introduction of  $Nd^{3+}$  into the garnet structure for doped level up to  $x=2$ , promoting a consistent increment in the lattice parameters with the  $Nd^{3+}$  content. For higher contents than  $x=2$  of  $Nd^{3+}$ , the garnet structure is transformed to orthoferrite phase. Besides, the magnetic results reveal an increase in the Curie temperature as the amount of  $Nd^{3+}$  increases, remaining constant the saturation magnetization, remanence and coercivity.

ID-458

**FePd magnetic nanoparticles by solid-state dewetting of thin films**G. Barrera<sup>1</sup>, F. Celegato<sup>1</sup>, M. Coisson<sup>1</sup>, M. Cialone<sup>1</sup>, P. Rizzi<sup>2</sup>, P. Tiberto<sup>1</sup><sup>1</sup> INRIM<sup>2</sup> Dipartimento di Chimica, Università di Torino

Magnetic particles of controlled size have raised a broad technological interest in different areas such as catalysis, photonics, sensing and for fabricating multifunctional magnetic systems. Solid-state dewetting is a promising thermally activated bottom-up method to pattern magnetic thin films into nanoparticles on a large scale. In dewetting method, the spontaneous agglomeration of a metallic thin solid film on a substrate into an assembly of particles with defined shape and size is a controllable process by means of different factors such as annealing parameters (temperature and time), substrate type and film composition and thickness.

In this work, magnetic FePd particles starting from a continuous film are obtained. The starting  $\text{Fe}_x\text{Pd}_{1-x}$  thin films are deposited on a silicon oxide substrate by rf-sputtering (film thickness about ranging from 6 to 100 nm) with nominal compositions having  $x = 70$  and  $80$ . To promote dewetting, the as-deposited thin films are subsequently submitted to a furnace annealing in vacuum atmosphere at selected temperatures (TA) in the range  $700 - 870^\circ\text{C}$  and for different time (tA) in the interval of  $0 - 100$  minutes. The dewetting process of FePd thin films has been carefully studied as a function of annealing temperature and annealing time. The process has been followed by acquiring scanning electron microscopy (SEM) images of annealed FePd samples to investigate the progressive steps of dewetting. This allows to analyze particle shape factors such as density, circularity and equivalent diameter. By finely tuning the annealing parameters and depending on film thickness, FePd nanoparticles having diameter varying in a wide interval have been obtained (30 – 300 nm).

Isothermal magnetic hysteresis loops have been measured in all studied samples by means of an alternating gradient force magnetometer (AGFM) to understand the evolution of magnetic properties, i.e. coercivity, initial susceptibility and remanence during the particles formation in the dewetting process. First Order Reversal Curves (FORCs) have also been performed in order to gain an insight on the irreversible magnetisation processes and to correlate them as a function of the progressive film nanostructuring during dewetting evolution. The contour plots demonstrate that upon completion of such a transformation, the magnetic measurements point to the development of a system composed of mostly non-interacting particles arrays.

## KEYNOTE LECTURE

Chair: A. Paolone

**H<sub>2</sub> Photo-generation promoted by iron oxide nanoarchitectures prepared by CVD-Based approaches**

C. Maccato

*Padova University, Italy*

The fossil fuels depletion and the concomitant pollution increase have boosted huge efforts devoted to the search of alternative and sustainable energy vectors. In this context, hydrogen represents an appealing alternative due to its high efficiency and clean combustion, but the development of environmental friendly H<sub>2</sub> generation routes still represents an open issue. To this regard, solar-assisted hydrogen production from water solutions by photo-activated processes has received a great attention as an amenable way to convert sunlight into storable chemical energy. In particular, the design of active photocatalysts endowed with tailored structure, morphology and composition is of utmost importance to gain appealing functional performances.

Among the possible active materials, iron oxide-based systems and, in particular, Fe<sub>2</sub>O<sub>3</sub>, stand as interesting photocatalyst thanks to their promising chemico-physical properties, encompassing low environmental impact, low cost, and favorable energy gap to harvest Visible light. Nevertheless, their performances are detrimentally affected by recombination losses, requiring the implementation of their structural, compositional and morphological properties in order to improve their functional behavior.

This contribution will provide a survey of recent studies conducted in our research group on photo-assisted H<sub>2</sub> generation by supported Fe<sub>2</sub>O<sub>3</sub>-based nanosystems obtained by Chemical Vapor Deposition (CVD)-based approaches. In particular, tailoring of the system nano-organization, structure and composition will be critically discussed in relation to the following case studies:

- i) anion-doped  $\alpha$ -Fe<sub>2</sub>O<sub>3</sub>, the most thermodynamically stable polymorph [1];
  - ii)  $\beta$ - and  $\epsilon$ -Fe<sub>2</sub>O<sub>3</sub>, two scarcely explored phases, used for the first time in the target application [2];
  - iii) Fe<sub>2</sub>O<sub>3</sub>/TiO<sub>2</sub> nanocomposites, eventually functionalized with Au nanoparticles [3].
- The role of the interplay between synthesis parameters, chemico-physical properties and functional properties will also be discussed.

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Wednesday 4 July afternoon - 15:30/17:00

Parallel Session 1  
**METALLIC GLASSES VIII**  
Chair: J. Bhatt

ID-117

**On the crystallization of a new high-entropy metallic glass studied by Mössbauer spectroscopy***S.L. Panahi, E. Pineda, P. Bruna**Departament de Física. Universitat Politècnica de Catalunya*

High-entropy alloys are defined as solid-solution alloys with five (or more) elements all them in equal (or near-equal) atomic percent. This type of alloys has led to a new design strategy for the development of new metallic materials with potential industrial applications due to their superior properties, like ultrahigh fracture toughness exceeding that of most pure metals and alloys, excellent strength comparable to that of structural ceramics, superconductivity or significant resistance to corrosion. In particular, in the field of metallic glasses (MGs), the appearance of some high-entropy metallic glasses (HEMGs) has introduced a new way to obtain new metallic glass-forming compositions. In-stead of tailoring the properties of MGs through microalloying, i.e. minor additions of elements with less than 1 or 2 at.%, the adequate design of a HEMG can combine the excellent properties of high-entropy alloys with the unique characteristics of MGs. The non-crystalline structure of MGs results in a large elastic region, ultrahigh strength as well as good soft magnetic properties. Moreover, the high-entropy alloy design strategy could lead to enhancements of the glass forming ability of some metallic glasses and the HEMGs can be an ideal model to investigate some fundamental issues such as the glass transition, the deformation mechanisms or the relaxation phenomena and aging in metallic disordered materials.

We have produced a new metallic glass composition with potentially good mechanic and soft magnetic properties, substituting the Fe in the  $\text{Fe}_{80}\text{B}_{20}$  composition by equal amounts of Fe, Co, Cr and Ni, to obtain a high-entropy metallic glass of composition  $\text{FeCoCrNiB}$ , maintaining the proportion of 80% of metal atoms and 20% of metalloid atoms. Moreover, as the addition of Si has been used to improve the corrosion behavior of some metallic glasses, a composition with a partial substitution of 10 at% of B by Si has also been produced. In this study, we characterize the thermal behavior of these alloys by means of DSC and we examine the changes in local order during structural relaxation and crystallization obtained by means of Mössbauer spectroscopy. Complementary studies of the mechanical and magnetic properties of these alloys have also been performed and correlated to the local microstructure of the amorphous and partially crystalline samples.

## ID-94

**HRTEM investigation of diffusion in glassy multilayer films**

*S. Ketov<sup>1</sup>, I. Ivanov<sup>2</sup>, D. Luzguine-Luzgin<sup>3</sup>, C. Suryanarayana<sup>4</sup>, L. Greer<sup>2</sup>, A. Chuvilin<sup>5</sup>, J. Eckert<sup>1</sup>*

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<sup>3</sup> *Advanced Institute for Materials Research, Tohoku University*

<sup>4</sup> *University of Central Florida, Department of Materials Science and Engineering*

<sup>5</sup> *CIC nanoGUNE Consolider*

Lack of plasticity is one of the main disadvantages of metallic glasses which can be solved by formation of composite materials. One of the promising ways to produce such materials is diffusion bonding. In the present work diffusion in the glassy multilayered film was investigated. Combination of advanced high resolution TEM methods and fine sputtering technique allowed to visualize and study diffusion in amorphous materials with high precision. Multilayered films were obtained by RF sputter deposition of Zr-Cu and Zr-Pd (5 layers of each composition) on SiO<sub>2</sub> substrate. The thickness of each layer was about 20 nm. This multilayer was capped from both sides by Ta for protection from oxidation and diffusion of Si into the film. Multilayered film was annealed in vacuum for 1 and 5 hours at sub-crystallization temperature of 400°C. The structure of the obtained films was investigated with high resolution transmission electron microscopy. It was observed that despite high annealing temperature, only copper diffuses across the boundaries of the layers. 1 hour of annealing results in formation of copper nanocrystals in the Zr-Cu layers. However, they disappear after 5 h of annealing. This effect was connected with redistribution of excess volume between the layers during annealing and Kirkendall voiding to favor formation of heterogeneous structure in Zr-Cu layers.

ID-227

**Fluctuation electron microscopy (FEM) of amorphous CuZr and nanocrystalline Cu nanolaminates***F.A. Davani, S. Hilke, M. Peterlechner, G. Wilde*

Metallic glasses are of interest due to their high strength and hardness. Upon deformation, it is expected that softer regions deform locally, finally leading to localized shear in so-called shear bands. In this work, multi-layers of amorphous CuZr and nanocrystalline Cu have been prepared by magnetron co-sputtering of pure Zr and Cu targets. Upon deformation of the layered system, the deformation can be analyzed in the crystalline and amorphous regions. Undeformed and deformed states were compared using conventional transmission electron microscopy (TEM) and scanning TEM (STEM) including high-angle annular dark-field (HAADF) analyses. Ensembles of the nanobeam diffraction pattern (NBDP) and energy dispersive X-ray (EDX) spectra were recorded with a nanometer probe size and small convergence angles. The NBDPs were analyzed according to variable resolution fluctuation electron microscopy (FEM), by plotting at a given probe size the normalized intensity variance as a function of the diffraction angle. Moreover, mappings of normalized variance were carried out. The processing, structure and the structure after deformation are analyzed. Structural changes upon deformation could be identified, however, local variations due to shear bands could not be measured. The results are discussed with respect to previous work and simulations.

## ID-124

**Measurement of glass transition temperature of metallic glasses using step-scan modulated temperature differential scanning calorimetry**

*P.P. Jana, J. Das*

Glass transition temperatures and crystallization temperatures of glassy ribbons and plates of  $Zr_{55}Cu_{30}Ni_5Al_{10}$  were measured using conventional differential scanning calorimetry (DSC) and step-scan modulated temperature differential scanning calorimetry (MTDSC). The glassy nature of the ribbons and BMGs has been studied using high-resolution transmission electron microscopy. No traces of crystallization have been observed in the glassy specimens under different processing conditions. Since, presence of higher free volume content in glassy ribbons is expected due to high quenching rate as compared to glassy plates, which has been assured from higher glass transition temperatures ( $T_g^{onset}$ ) of MG ribbon samples in DSC and step-scan MTDSC analysis. A large scatter of  $T_g^{onset}$  ( $\pm 14.8$  K) has been estimated using DSC technique for both as spun ribbon and as cast plate samples, while a more precise estimation of  $T_g^{onset}$  ( $\pm 1.3$  K) can be accessed using step-scan MTDSC from the reversible heat flow curve. The  $T_g^{onset}$  value of differently processed ribbons and plate samples decreases pointing a decrease of free volume.

Keywords: Metallic glass; Differential scanning calorimeter; Glass transition temperature; Free volume

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## ID-30

**In-situ Ta particle reinforced Zr-based bulk metallic glass matrix composites**

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<sup>2</sup> Tohoku University, Japan

The room-temperature brittleness of most bulk metallic glasses (BMGs), which results from the localized deformation in shear bands (SBs), limits the widespread applications of them [1]. Introducing a crystalline secondary phase to fabricate the BMG matrix composites (BMGMCs) is proved to be an efficient way to improve the ductility of BMGs [2]. In the present study, we have successfully introduced the in-situ ductile Ta particles into a  $Zr_{55}Cu_{30}Ni_5Al_{10}$  (at.%) BMG by minor alloying with 7, 9 and 10 at.% Ta, denoted as Ta7, Ta9 and Ta10, respectively. The microstructure and mechanical properties are investigated in detail.

To fabricate the master alloy, two step arc-melting was used. Firstly, the Ta–Zr solid-solution pre-cursor was prepared because of the high melting temperature of Ta. Then the Ta–Zr precursor was melted with remaining Cu, Al, Ni pieces. The BMGMC specimens were produced by the injection copper mold casting. The structure of the specimens was examined by XRD, SEM and TEM. The glassy transition temperature ( $T_g$ ) and the onset crystalline temperature ( $T_x$ ) were measured by DSC. Uniaxial compressive and tensile tests were performed at a strain rate of  $5 \times 10^{-4} \text{ s}^{-1}$  at room temperature.

The in-situ Ta particle has been successfully introduced into the Zr-based BMG matrix by doping Ta. With more Ta doping, more particle precipitates. The volume fraction of Ta particles for Ta7, Ta9 and Ta10 are 5%, 12% and 15%, respectively. The interfaces between Ta particles and BMG matrix seems to be distinct, including a gradient transformation from crystalline ordering fringe of Ta to the maze characteristic of amorphous phase. The composites show remarkable plasticity during compression, e.g., 34.7% plastic strain for Ta10. With more Ta particles, the composites show a higher plastic strain. Furthermore, Ta10 even shows 2.1% plastic deformation during tension. The Ta particles are considered to hinder the rapid propagation of main shear band, causing it stopped, branched or multiplied. Moreover, the deformation of Ta particle itself also contributes to the overall plasticity by lowering the stress concentration at the interfaces. The present BMGMCs are considered to be a good candidate as engineering materials.

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## ID-90

**3D printing of Fe-based bulk metallic glass and composites with large dimensions and enhanced toughness by HVOF thermal spray**L. Liu*Huazhong University of Science and Technology, China*

Fe-based bulk metallic glasses (BMGs) with high strength and outstanding corrosion resistance are desirable for structural and functional applications. However, size limitation and extreme brittleness block the applications of these materials. Here we presented a novel approach, namely thermal spray 3D printing (TS3DP), to fabricate large-size Fe-based BMG and BMG composites (BMGCs). It was found the TS3DP technique can easily produce large size Fe-based BMGs (theoretically without size limitation) with nearly fully amorphous structure and enhanced toughness, which was twice higher than that of the as-cast BMG with the same composition. More importantly, this approach allows an easy fabrication of Fe-based BMG composites with desirable microstructure and mechanical properties by simply using the mixtures of Fe-based amorphous powders and other crystalline particles. Taking the advantage of this peculiarity, we have successfully prepared Fe-based BMG composites reinforced with various fractions of stainless steel particles through TS3DP. These composites exhibited high strength of 1.8–2.0 GPa and fairly good fracture toughness (KJ) of 16–21 MPa m<sup>1/2</sup>. The toughening mechanisms were investigated in terms of structure and stress field distribution under external loading based on finite element modelling. It was revealed that the high toughness of the TS3DP BMG composite benefited from the unique layered microstructure and stress shielding effect caused by the ductile stainless steel phase, which consequently led to significant crack deflection and high fracture energy dissipation. The present work provides an avenue to the fabrication of large size BMGs and BMG composites with enhanced mechanical properties for structural applications.

**Wednesday 4 July afternoon - 15:30/17:00**

Parallel Session 2  
**NANOSTRUCTURED MATERIALS VIII**  
Chair: M.D. Baro'



**ID-450 (Invited)****Pseudo-morphic transformation of nanocrystals by element replacement**

*T. Teranishi, R. Sato*

*Kyoto University*

Chemical conversion of inorganic nanocrystals (NCs) via element replacement reactions, such as ion exchange reactions and galvanic replacement reactions, can overcome the difficulties associated with controlling the size, shape, chemical composition, and crystal structure in conventional syntheses. The retained shape of the parent-NCs in element replacement reactions provides an opportunity to obtain non-equilibrium unique structures and even new structures of inorganic NCs, these final structures being known as “pseudomorphs” [1-4]. Here I present the nano-pseudomorphic chemistry to give unique semiconductor [5] and metallic NCs [6]. Novel structure-specific optical properties of the obtained NCs will be also presented [7].

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[5] H.-L. Wu, T. Teranishi et al., Science 2016, 351, 1306.

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[7] R. Sato, T. Teranishi et al., to be submitted.

## ID-155

**Solution combustion synthesis of nanostructured non-oxide materials: alloys, intermetallics, nitrides**

*S. Roslyakov<sup>1</sup>, C. Chuck<sup>2</sup>, A. Mukasyan<sup>2</sup>*

<sup>1</sup> National University of Science and Technology MISIS

<sup>2</sup> University of Notre Dame

During the last three years, the SCS field has experienced an explosion of interest with more than hundreds articles published. The published papers are related to different science and engineering disciplines, including synthetic inorganic chemistry and electrochemistry, chemical and electrical engineering, bio- and materials science. Such rapid success in a variety of applications became possible due to recent breakthroughs in understanding of fundamental mechanism of structure and phase formation during SCS that allowed to synthesize several transition metals (Ni, Cu, Co) and alloys (CuNi, NiCo). It is shown that the combustion of nickel (and/or copper) nitrate and glycine mixture at near-stoichiometric and fuel-lean conditions indeed produces fine oxide powders. However, excessive quantities of fuel lead to the formation of pure metal or alloy. A new class of metal-based materials produced by SCS opens vast opportunities for this flexible method to synthesize a wide range of compounds with tailored nanostructures and properties. In the present work, we report about new phases such as nitrides ( $\text{Fe}_3\text{N}$ ), carbonitrides ( $\text{Fe}_3\text{N}_{1-x}\text{C}_x$ ), bimetals (FeNi-, FeCu-, FeCo-, NiAl- alloys) and high entropy alloys obtained during solution combustion process under different synthesis conditions.

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ID-209

**Grain growth kinetics in  $\text{Al}_x\text{CoCrFeNi}$  ( $x=0, 0.3, 0.6, 1$  mol) high entropy alloy synthesized through mechanical alloying***M.M. Garlapati, B.S. Murty**Indian Institute of Technology Madras*

Grain growth kinetics in  $\text{AlCoCrFeNi}$  high entropy alloy (HEA) by varying concentration of Al has been studied. Nanocrystalline HEAs are synthesized through mechanical alloying in a high-energy ball mill with crystallite sizes of less than 10 nm. Nanocrystalline powders are heat treated at different temperatures (673, 873 and 1073 K). X-Ray diffraction and transmission electron microscopy have been used for phase identification and crystallite size measurement. The composition of as milled and heat treated powders was analysed using energy dispersive spectroscopy attached to a scanning electron microscope. Phases starting from single phase fcc to major bcc phase were observed from lower Al content to the concentration of 1 mol, respectively. Mixture of fcc and bcc is observed at intermediate concentrations (0.3, 0.6 mol). Power law has been used to calculate grain growth kinetics. The activation energy for grain growth and grain growth exponent ( $n$ ) have been calculated. Variation in the measured values has been compared to the stability of phases after heat treatment. Grain growth exponent ( $n$ ) and activation energy ( $Q$ ) come out to be 3.8 and 315 kJ/mol in equiatomic  $\text{AlCoCrFeNi}$  and is observed to vary with Al concentration.

## ID-215

**Shape controlled synthesis of Au-Cu bimetallic nanostructures**

*M.K. Singh, J. Basu, B. Mukherjee, R.K. Mandal*

<sup>1</sup> IIT(BHU), Varanasi

The combination of gold and copper is a potential way to reduce the cost of metallic interconnects and ameliorate the instability of copper. Synergy of these two metals can be exploited in a better fashion through shape controlled synthesis. The phase diagram of Au-Cu is complex in nature with appearance of several intermetallics such as Au<sub>3</sub>Cu, AuCu and AuCu<sub>3</sub> at lower temperatures (~400°C). In addition to that, alloying behaviour of Au-Cu is not understood well, when the temperature is lowered down further. In this study, Au-Cu bimetallic nanostructures have been synthesized by wet chemical route wherein HAuCl<sub>4</sub>·3H<sub>2</sub>O and CuCl<sub>2</sub>·2H<sub>2</sub>O were co-reduced by glucose in aqueous solution in the presence of long chain amines (hexadecylamine and octadecylamine) at 100°C. By changing the synthesis conditions, nanostructures of various shapes such as nanowires, multi-ply twinned tripod, tetrapod, etc. were observed. Systematic variation of the syntheses condition not only lead to a change in size and morphology but also various other crystallographic features develop in the nanostructures. Samples were collected at different stages to understand the growth mechanism of the resultant nanostructures. It has been observed that nanostructures are composed of homogeneous Au-Cu alloy as revealed by STEM-EDS results. To understand the alloying behavior and underlying chemistry of Au-Cu nanostructures, attempts have been made to quantitatively understand the contrast and its interpretation in terms of atom column positions of Au and Cu of high resolution phase contrast images. Multislice image simulations were performed with varying thickness and defocus values and they were matched with the experimentally obtained high resolution phase contrast images. HRTEM results showed twin boundaries and stacking faults in the Au-Cu nanostructures. The formation of nanowires and branching in nanostructure under the present synthesis condition have been explained in terms of oriented attachment kinetics of Au-Cu nanocrystals. Multiply twinned branched shape Au-Cu (width of branch ~30 nm) products display strong localized surface plasmon resonance peaks in the near-infrared region which may provide an avenue for their potential applications in photothermal therapy. Further, observed change in microstructural features leading to exposure of areas with active sites may be helpful for enhancing catalytic activities of these class of materials.

ID-303

**Liquid state amorphization of interphases in metal-silicon couples**

R. Walser

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Reactions of all noble, near noble, lanthanides, and transition metals deposited on crystalline Si substrates have been observed at  $\leq 300\text{K}$ . High resolution XTEM shows that the initial structure of the interfaces of all refractory metals, platinum-group metals, and some rare-earth metals, with crystalline Si substrates, is an amorphous interphase (AIP) a few nm thick. AIPs are doorway states to reaction paths of interfaces used in some of the most important areas of technology. They were assumed to exist 40 years ago [1] but detected 15 years later [2]. The AIP is thought to be generated by a solid state amorphization (SSA) resulting from a diffusional reaction [3]. In SSA, layer growth of the AIP is driven by heat released in M-Si reactions. Several aspects of SSA are not consistent with reaction paths reported for many M-Si couples that form AIPs. Prior to forming an AIP, reconstructed interface layers (RILs) form from 1-2 monolayers of deposited metal. In couples where M-M bond formation is more favorable than the formation of M-Si bonds, additional metal deposition nucleates metal nano-islands. The growth of the planar RIL, and the subsequent island growth is a Stranski-Krastanov process typical for the majority of M-Si couples.

We model a liquid state amorphization (LSA) of the AIP quenching a localized Si melt. LSA is driven by a phonon pulse generated by collective inelastic electron tunneling through the RIL, triggered by quantum percolation of metal nano-islands. At percolation, tunneling is initiated when the ionization energy of isolated metal nano-islands jump from well above, to below the Si work function. All AILs have a quasi-2D thickness of  $\sim 10\text{-}30$  monolayers. The AIL is assumed to form by quenching a localized, low dimensional melt, at temperatures typically about  $\frac{1}{2}$  that of bulk Si. To reach this T, and localize the melt energy in a nanometric region, tunneling electrons are inelastically transferred to a short pulse of Si lattice phonons with high peak energy. A phonon pulse initiated by quantum percolation could turn on in  $< 1$  ps and rapidly relax in a few ps by transport. In LSA, AILs form by quenching low dimensional M-Si eutectic melts at  $\sim \frac{1}{2}$  their eutectic temperatures. Binary phase diagrams confirm that these results agree with the model in [1].

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Wednesday 4 July afternoon - 15:30/17:00

Parallel Session 3  
**MATERIALS FOR RENEWABLE ENERGY VI**  
Chair: S. Nakamae

**ID-283 (Invited)****Effect of non-equilibrium processing on the synthesis and thermoelectric properties of skutterudites and half Heusler compounds**

A. Castellero<sup>1</sup>, F. Aversano<sup>1</sup>, S. Branz<sup>1</sup>, C. Artini<sup>2</sup>, A. Ferrario<sup>3</sup>, S. Boldrini<sup>3</sup>, C. Fanciulli<sup>4</sup>, M. Baricco<sup>1</sup>

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Thermoelectric materials have attracted great attention because of their use for direct electrical power conversion from exhaust or waste heat sources, resulting in improved energy efficiency [1]. Since thermoelectric properties (Seebeck coefficient, electrical conductivity and thermal conductivity) are strongly correlated to the electronic structure of a given system, thermoelectric performance can be enhanced by chemical doping in the material and by decoupling electron and phonon scattering through microstructural defects [2].

Beside their thermoelectric properties, skutterudites and half Heusler compounds are the most promising candidates for commercial applications in the medium temperature range (400-600°C) because they are not based on critical raw materials. Melt processing of skutterudites and most of half Heusler compounds is usually inhibited by peritectic reactions that require extremely long annealing to form the desired phase [3,4].

In this work, we explored the effect of non-equilibrium processing techniques, such as rapid solidification and mechanical alloying, on the synthesis, structural, microstructural and thermoelectric properties of representative skutterudites and half Heusler compounds.

In Yb-filled CoSb<sub>3</sub> skutterudite, rapid solidification produces a fine microstructure that induces a faster homogenization and Yb filling because of the increased grain boundary diffusion.

In the case of Sm-filled Fe<sub>2</sub>Ni<sub>2</sub>Sb<sub>12</sub> skutterudite [5] and TiNiSn half Heusler compound [6] rapid solidification allows to form directly the desired phase bypassing equilibrium peritectic reactions due to the undercooling of the liquid, as shown by the comparison between equilibrium and metastable phase diagrams calculated by CALPHAD. Furthermore, rapid solidification leads to supersaturation of Ni in TiNiSn and, consequently, decreased lattice thermal conductivity.

Mechanical alloying of TaCoSn, that cannot be processed in the molten state due to difference in melting temperature of Ta and Sn, leads to amorphization of the alloy. Subsequent crystallization of the metastable amorphous phase produces the stable half Heusler structure.

Thermoelectric properties of the massive samples, obtained by sintering of crushed ribbons and mechanically alloyed powders, are discussed in term of structural and microstructural features.

## Acknowledgements

Alberto Castellero thanks Fondazione CRT (Grant N. 2015.1530), Compagnia di Sanpaolo and University of Turin (Project number CSTO162398) for financial support.

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ID-369

**Augmented thermoelectric power generation in ferrofluid based thermoelectrochemical cells**

*K. Bhattacharya, T. Salez, M. Bonnet, M. Roger, C. Guibert, V. Peyre, E. Dubois, R. Perzynski, E. Laux, L. Jeandepoux, H. Keppner, S. Nakamae*

Low-grade waste heat generated from industrial setups, geothermal activities, solar heating etc., is considered as a prospective contender in the continual quest for sustainable energy sources [1]. Presently, semiconductor based solid-state thermoelectrics is preferred to tap into this source of sustainable energy by directly converting low-grade heat into electrical energy [2]. Despite recent advances in solid-state thermoelectric materials via nanostructuring, their efficiency is still limited by various factors such as high material and processing cost, limited efficiency at low temperatures etc [3]. In recent times, liquid based thermoelectrochemical cells are coming up as an attractive alternative for low-grade waste heat harvesting due to their simple design, cost effectiveness and environmentally benign nature [4,5].

The present work demonstrates an innovative method for augmenting the performance of thermoelectrochemical cells by incorporating charged and magnetic colloidal nanoparticles into host liquid electrolytes (i.e., ferrofluids). In this work, we studied the Seebeck coefficient of ferrofluid-based thermoelectrochemical cells, and how the thermodiffusion of nanoparticles can effectively enhance the power output near room temperature. Additionally, the effect of anisotropic magnetic nature of the nanoparticles on the power generation was studied. Our current theoretical interpretation of the observed phenomena as well as the prospective on future thermoelectrochemical research on colloidal and magnetic fluids will also be discussed.

This work is supported by European Union's Horizon 2020 research and innovation programme under the grant agreement No 731976 (MAGENTA).

ID-321

**Role of Ta in improving thermoelectric properties of nanocrystalline  $Ti_{1-x}Ta_xNiSn$  ( $x=0, 0.01, 0.03, 0.05$ ) alloys synthesized by mechanical alloying***A. Karati<sup>1</sup>, R.C. Mallik<sup>2</sup>, R. Shabadi<sup>3</sup>, U.V. Varadaraju<sup>1</sup>, B.S. Murty<sup>4</sup>*<sup>1</sup> *Department of Chemistry, Indian Institute of Technology Madras, Chennai 600036, India*<sup>2</sup> *Thermoelectric Materials and Devices Laboratory, Department of Physics, Indian Institute of Science, Bangalore 560012, India*<sup>3</sup> *Faculty of Science and Technology, UMET, University of Lille, Villeneuve-d'Ascq, France*<sup>4</sup> *Department of Metallurgical & Materials Engineering, Indian Institute of Technology Madras, Chennai 600036, India*

Thermoelectric materials are used in devices that convert waste heat into electricity. They have found application in the field of power generation and refrigeration over the last few decades. Thermoelectric materials should possess a high Seebeck coefficient (S), high electrical conductivity ( $\sigma$ ) and low thermal conductivity ( $\kappa$ ) to attain a high thermoelectric figure of merit  $ZT=(S^2\sigma/\kappa)T$ . High values of ZT have been exhibited by  $Bi_2Te_3$  based materials in the room temperature region (up to 350 K), PbTe based and skutterudites in the middle temperature region (400-800 K) and SiGe based systems in the high temperature region (900 K and above). Heusler materials fall in the category of high ZT materials in the mid to high temperature region i.e. 700-1000 K.

Half-Heusler materials are ternary intermetallic compounds that adopt the MgAgAs structure. They consist of four interpenetrating fcc sub-lattices. The three constituent elements form the three sub lattices and the fourth sub-lattice is empty. Heusler compounds with VEC=18 are semiconducting and compounds such as TiNiSn (n-type) and TiCoSb (p-type) are well known thermoelectric materials. Partial or complete substitution of heavy atoms (Zr and Hf) in Ti, micro-scale and nano-scale Heusler matrix with nano-scale inclusions are some of the strategies that have been employed to enhance the ZT in Heusler materials.

In the present work, TiNiSn alloy was synthesized by mechanical alloying followed by spark plasma sintering (MASPS) and it yielded a ZT of 0.14 at 800 K. This is the highest recorded figure of merit observed in TiNiSn synthesized by MASPS route. The improved property could be attributed to improved densification in the present alloy. Additionally,  $Ti_{1-x}Ta_xNiSn$  ( $x = 0.01, 0.03, 0.05$ ) alloys were synthesized by MASPS route. Upon doping Ta in the Ti center, a dual improvement in densification and thermoelectric figure of merit was observed. The highest ZT of 0.29 was observed at 800 K for  $x = 0.05$  alloy. The results would be compared with cast alloys to understand the influence of nanocrystallinity in these alloys.

ID-429

**Highly efficient and facile PEDOT:PSS-based thermoelectric materials doped with single walled carbon nanotubes***K. Yusupov, A. Vomiero<sup>1</sup>, D. Hedman<sup>1</sup>, V. Khovaylo<sup>2</sup>, A. Larsson<sup>1</sup>, S. You<sup>1</sup>, A. Nasibulin<sup>3</sup>, A. Tsapenko<sup>3</sup>*<sup>1</sup> Lulea Technical University<sup>2</sup> National University of Science and technology "MISiS"<sup>3</sup> Skolkovo Institute of Science and Technology

Currently, the scientific community put a lot of effort to investigate alternative sources of energy. Emphasis deserves green energy sources, such as solar energy, water energy, etc. Among them, thermoelectric (TE) materials, which allow the direct conversion of heat energy into electricity are highly promising. Apart from the traditionally used semiconducting alloys for which high figure of merit values were achieved ( $ZT = (\sigma \cdot S^2) / T \cdot k$ , where  $\sigma$  is the electrical conductivity,  $S$  the Seebeck coefficient,  $T$  the temperature, and  $k$  the thermal conductivity), polymers have been considered as promising TE materials due to the simple synthesis methods, non-toxicity, low thermal conductivity, and electrical conductivity etc. Thus, mentioned making polymers good candidates as TE materials. However, polymers exhibit some disadvantages: small  $\sigma$  and  $S$ , which should be overcome for successful utilization in TE field. For example, a considerable increase in electrical conductivity has been achieved in polymer composites by introducing carbon nanotubes (CNTs) into a polymer matrix. However, due to the natural hydrophobicity of CNTs, they tend to form agglomerates within the composite samples during the obtaining process, such lead to inhomogeneity and, as a result, in a high anisotropy of properties. In the present work, we studied the influence of single-walled CNTs on thermoelectric properties of the polymer matrix. Instead of dispersing CNTs within the matrix, the tubes were covered with the polymer matrix without changing the original structure, i.e. the tubes were manufactured by chemical vapor deposition method with further uncontrollable falling on the substrate (lead to low anisotropy), then the SWCNTs were covered with the conductive polymer via the spin-coating process.

The target of the work was to enhance the  $\sigma$  and to improve the homogeneity of the composites. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) was used as the polymer matrix. Samples were examined with SEM, Raman and EDX analyses to clarify differences in morphology/composition. Transport properties ( $\sigma$  and  $S$ ) were measured by a standard four-probe method. The study of formed SWCNTs exhibited no presence of agglomerates. This feature improved reproducibility of measurements and increased the electrical conductivity. Obtained samples even without any additional doping or post-treatment exhibited outstanding power factor values ( $\sigma \cdot S^2$ ), the highest of which is 205 W/K<sup>2</sup>m.

Wednesday 4 July afternoon - 15:30/17:00

Parallel Session 4  
**MAGNETIC, TRANSPORT AND OPTICAL PROPERTIES FROM  
NANOSCALE TO BULK III**  
Chair: R. Mathieu

**ID-164 (Invited)****Engineering of magnetic properties and GMI effect in Fe-rich magnetic microwires by stress annealing**

*A. Zhukov<sup>1,2</sup>, P. Corte-León<sup>3</sup>, M. Ipatov<sup>1</sup>, J.M. Blanco<sup>3</sup>, M. Churyukanova<sup>4</sup>, V. Zhukova<sup>1</sup>*

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Recently studies of amorphous magnetic wires attract great attention owing to excellent magnetic properties such as magnetic bistability, excellent magnetic, mechanical and corrosion properties, Giant Magnetoimpedance (GMI) effect [1]. A fore-mentioned GMI effect consisting of a large change of the impedance of a magnetic conductor under magnetic field is quite interesting for magnetic sensors applications [2]. Recent tendency in devices miniaturization stimulated development of thin (few micrometers diameters) soft magnetic microwires prepared using Taylor-Ulitovsky method. Excellent soft magnetic properties and GMI effect have been reported for properly prepared and processed Co-rich microwires [1]. Less expensive Fe-rich microwires are preferable for the applications. But amorphous Fe-rich materials exhibit rather high magnetostriction coefficient and consequently present quite low GMI effect [1]. The most common method for magnetic softness optimization is the annealing. Nevertheless, recently the optimization of soft magnetic properties and GMI effect after are reported mostly for brittle devitrified Fe-rich microwires [1]. From previous studies of Co-rich amorphous materials, it is known that stress annealing can considerably affect the magnetic properties of amorphous materials [1].

Consequently, the purpose of this paper is to present our recent experimental results on influence of stress- annealing on magnetic properties and GMI effect of Fe- and Fe-Co based glass-coated microwires. We observed that Fe-rich microwires annealed under stress at appropriate annealing conditions (time and temperature) can present low coercivity, considerable magnetic softening and enhanced GMI effect. Coercivity, remanent magnetization, magnetic anisotropy field and hence GMI-ratio values depends on temperature and time of stress-annealing, stress applied during the annealing [3]. For interpretation of observed changes, we considered internal stresses relaxation and different mechanisms of stress-induced anisotropy. Observed versatile properties of stress annealed glass-coated microwires with enhanced soft magnetic properties and GMI ratio make them suitable for industrial applications.

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## ID-225

**Development of magnetic anisotropy in CoO/Fe (001) by bottom-up interface engineering**

A. Brambilla<sup>1</sup>, A. Picone<sup>1</sup>, D. Giannotti<sup>1</sup>, H. Hedayat<sup>1</sup>, E. Carpena<sup>2</sup>, C. Dallera<sup>1</sup>, G. Vina<sup>3</sup>, P. Torelli<sup>3</sup>, M. Foerster<sup>4</sup>, L. Aballe<sup>4</sup>, M. Finazzi<sup>1</sup>, D. Lamberto<sup>1</sup>, F. Ciccacci<sup>1</sup>

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Intriguing magnetic properties can be obtained in systems containing antiferromagnetic (AF) transition metal (TM) oxides (O) both by low-dimensionality and by proximity to ferromagnetic (F) layers. So far, we have investigated both chemical [1] and magnetic [2] properties of a variety of Fe/AF (NiO, CoO) layered structures. One of the most critical issues concerning reactive TMO/TM interfaces is the high degree of chemical mixing [1]. Exploiting a metastable Co buffer layer, we have succeeded in obtaining a CoO/Fe interface free of any Fe oxide that, intriguingly, is also characterized by a dislocation-driven nanostructuring of CoO, which grows in three-dimensional regularly arranged square islands, whose lateral sizes increase with CoO coverage, up to some tens of nanometers [3]. Such an interface engineering leads to the development of a significant uniaxial magnetic anisotropy, induced by tiny amounts of deposited CoO [4]. The corresponding magnetic behavior and the physical mechanisms that drives it were investigated by standard (magneto-optical Kerr effect, MOKE) and element specific (X-ray Magnetic Circular Dichroism, XMCD) hysteresis loops, by magnetization-induced second harmonic generation (MSHG), and by XMCD-Photoelectron Emission Microscopy (XPEEM) revealing that the source of the magnetic anisotropy resides indeed at the very interface of the system.

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ID-443

**Effect of H<sup>+</sup> irradiation on magneto-optical properties of Co-doped ZnO thin films***A. Di Trollo<sup>1</sup>, G. Varvaro<sup>1</sup>, A. M. Testa<sup>1</sup>, A. Polimeni<sup>2</sup>, F. Pineider<sup>3</sup>, C. Fernandez<sup>4</sup>, G. Barucca<sup>5</sup>, P. Mengucci<sup>5</sup>*<sup>1</sup> CNR-Istituto di Struttura della Materia<sup>2</sup> Dipartimento di Fisica, Università di Roma "La Sapienza"<sup>3</sup> Dipartimento di Chimica e Chimica Industriale, Università di Pisa<sup>4</sup> CNR-Institute of Materials for Electronics and Magnetism<sup>5</sup> Dipartimento di Scienze e Ingegneria della Materia, dell'Ambiente ed Urbanistica – SIMAU, Università Politecnica delle Marche

We present an investigation on the strong magneto-optical response exhibited by ferromagnetic Co-doped ZnO films upon hydrogen ions irradiation. Magneto-optical thin film materials with high figure of merit (i.e. high ratio of Faraday rotation per unit length to the optical loss per unit length) can pave the way for development of new integrated on-chip non-reciprocal photonic devices. Most efforts are currently directed to the growth of films of ferromagnetic garnet oxides which are however very difficult to integrate in optoelectronic technologies. In such a context, we show that ZnO-based diluted magnetic semiconductors obtained by incorporating transition metal elements (e.g. Fe, Co) are suitable for the purpose. Ferromagnetic behaviour of Co-doped ZnO films can be improved when treated by a suitable atomic hydrogen treatment [1]. We investigated the role of hydrogen in the improvement of the magneto-optical properties by comparing the magnetic circular dichroism spectra of H-irradiated ZnCoO films. Optical and microstructural analyses indicate that Co fully substitutes for Zn ions without phase segregation. In addition to a large increase in the saturation magnetization we observe larger values of the magnetic circular dichroism upon hydrogen incorporation, especially for the samples processed with high H-doses which also show a large value of the Faraday rotation at magnetic saturation.

These results give a direct indication of the intrinsic nature of the ferromagnetism in this class of materials as arising from the spin polarized carriers magnetically coupled to Co ions. The values of the Faraday rotation and hence the figure of merit of the hydrogenated films in the vis range can be tuned by a suitable choice of the H-dose and are promising in the perspective of non-reciprocal magneto-optical devices integrated on semiconductors.

[1] A. Di Trollo et al., ACS Appl. Mater. Interfaces 2016, 8, 12925.

## ID-300

**Metastable (Mn,Ti)Bi intermetallic: magnetic properties and thermal stability**

*E.S. Olivetti<sup>1</sup>, C. Curcio<sup>2</sup>, A. Bartok<sup>3</sup>, M. LoBue<sup>3</sup>, L. Martino<sup>1</sup>, V. Basso<sup>1</sup>*

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<sup>3</sup> SATIE, ENS Cachan, CNRS, Université Paris-Saclay

The MnBi intermetallic compound is a magnetic material with several intriguing features: a) the  $\alpha$ -phase exhibits a spin reorientation transition at low temperature and a large uniaxial anisotropy with a positive temperature dependence up to 500 K; b) at 628 K the  $\alpha$ -phase undergoes a first order magnetostructural transition from a ferromagnetic to a paramagnetic hexagonal structure, involving: Mn atoms migration, c-axis contraction and a-axis expansion ( $\beta$ -phase); c) upon quenching, the changes in cell constants and atom distribution can be partially frozen in, resulting in a lattice distortion from the hexagonal NiAs-type structure to an orthorhombic superstructure (quenched  $\beta$ -phase). This metastable phase is ferromagnetic at room temperature and possesses a magnetocrystalline anisotropy even larger than the one of the  $\alpha$ -phase, ( $K_u \beta = 2.9 \cdot 10^6 \text{ Jm}^3$  and  $K_u \alpha = 1.4 \cdot 10^6 \text{ Jm}^3$  at 300 K).

Substitutions of Mn with other transition elements have been attempted in order to stabilise the quenched  $\beta$ -phase in thin films samples. Besides, owing to the large magnetocrystalline anisotropy of both phases and to the entropy change of the magnetostructural transition ( $20 \text{ Jkg}^{-1}\text{K}^{-1}$ ), ternary Mn-Bi-based bulk materials are worth to be studied, with the aim of tailoring the magnetic properties and transition temperatures through composition, for potential applications in rare-earth-free permanent magnets or as magnetocaloric materials.

In this work we explored the role of Ti substitution on the microstructure, thermal stability and magnetic properties as a function of temperature (50–650 K) of (Mn,Ti)Bi polycrystalline samples obtained through rapid quenching from the melt (suction casting, mould casting and planar flow casting). Combined investigations, carried out by means of X-ray diffraction, magnetometry, differential scanning calorimetry and scanning electron microscopy, show that a metastable (Mn,Ti)Bi phase can be quenched more easily than the pure  $\beta$ -MnBi and has the following features: a) it is paramagnetic at room temperature but becomes ferromagnetic at 180 K; b) similarly to quenched  $\beta$ -MnBi it exhibits a negative temperature coefficient of coercivity; c) upon annealing it is stable up to 450 K, where it begins to transform into a  $\alpha$ -like (Mn,Ti)Bi phase; subsequently (580 K) Ti atoms are expelled from the cell and a pure  $\alpha$ -MnBi is recrystallised.



ID-308

**Magnetic properties of Fe-Ni permalloy produced with selective laser melting***A. Mazeeva, V. Bobyr, S. Manninen, M. Staritsyn, P. Kuznetsov*

The actual problem for today is the miniaturization of the elements of engineering and electrical devices and systems. The designs of magnetic, electronic, electro-technical, navigation and other systems are constantly becoming more complex. The precision alloys with special physical properties used for their manufacture play an important role. They can serve as source, amplifier or filter of the main signal, which drives the whole system and determines its accuracy and reliability. However, in the manufacturing of miniature components of complex geometry from the precision alloys, a number of problems arises: difficulties of using traditional machining to obtain a high accuracy degree and degradation of structurally sensitive properties under mechanical deformations. A prospective method to solve these problems is additive manufacturing after assumed 3D models.

Despite the obvious advantages, the application of additive manufacturing for producing parts from precision alloys is not wide at the present moment. This is due to the fact that the structure formation patterns, physical and mechanical properties of precision alloys, in particular of magnetic ones, produced by additive methods have not been fully studied yet. Though the latest publications show the greatest interest of researchers and large corporations in additive manufacturing parts for aviation, space technology, engineering, etc., and also in widening the directions for its new application in order to obtain a significant effect as well. In this sense the wide used precision magnetic alloys such as permalloys are of undoubted interest.

In this paper permalloy 50N was investigated. Since the initial material for the producing the items by AM-technologies is a metal powder, it was decided to include this step as well as subsequent thermal treatment of the product to the general technological scheme. The initial powders were obtained by gas atomization method. Their particle size distribution and particle shape were estimated and the fraction of less than 80  $\mu\text{m}$  was selected. Then the ring samples for magnetic properties measurements were manufactured with using the selective laser melting by means of EOSINT M270 according to determined technological regimes. The obtained results for magnetic permeability show the opportunity of stable physical properties formation for the selected precision alloy that is of great importance for the further industrial application.

Wednesday 4 July afternoon - 17:30/18:30

Poster Session 3  
**MATERIALS FOR RENEWABLE ENERGY**  
Chair: D.M. Trucchi

ID-32

**Catalytic performance of alloyed PtPdNi ternary as electrocatalysts for the methanol oxidation in alkaline medium***E. Ramírez-Meneses<sup>1</sup>, J. De La Cruz-Cruz<sup>2</sup>, M. A. Domínguez-Crespo<sup>3</sup>*<sup>1</sup> *Universidad Iberoamericana*<sup>2</sup> *Instituto Politécnico Nacional*<sup>3</sup> *Instituto Politécnico Nacional*

Different ternary PtPdNi alloys were synthesized by displacement of ligands from organometallic compounds method as electrode materials for the methanol oxidation in an alkaline medium, in order to evaluate the influence different the addition of Ni to binary  $Pt_xPd_{1-x}$  alloys. The alloys were synthesized at room temperature under  $H_2$  atmosphere at 3 Bar as reducing agent, tetrahydrofuran anhydrous as dissolvent, and using octylamine as stabilizer. The electrode materials were characterized by transmission electron microscopy (TEM), X-ray diffraction patterns (XRD) and X-ray photoelectron spectroscopy (XPS). The electrochemical performance of the ternary alloys toward methanol oxidation reaction (MOR) in 30 wt% KOH was evaluated by cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS) and chronoamperometry (CA) techniques. Results showed that ternary alloys displayed methanol oxidation currents higher than individual and binary alloys, which suggested that Ni addition promotes catalytic properties of Pt. The findings of the work indicate that these ternary alloys can be used to design highly effect anodic catalysts of direct methanol fuel cells.

ID-74

**Effects of friction stir processing on hydrogen storage of ZK60 alloy***E. Pereira da Silva<sup>1,2,3</sup>, D. R. Leiva<sup>1</sup>, H. Cavalcanti Pinto<sup>2</sup>, R. Floriano<sup>3</sup>, A. M. Neves<sup>1</sup>, W. J. Botta<sup>1</sup>*<sup>1</sup> *Department of Materials Engineering, Federal University of São Carlos, São Carlos, Brazil*<sup>2</sup> *São Carlos School of Engineering, University of São Paulo, Department of Materials Engineering, São Carlos-SP, Brazil*<sup>3</sup> *School of Applied Sciences, State University of Campinas, Limeira, 13484-350, SP, Brazil.*

In this paper we report the use of a novel processing route to produce samples for using as hydrogen carrier. ZK60 alloy was produced by induction melting and sheets taken from the melt ingot were submitted to Friction Stir Processing (FSP) and subsequent manual filing with a rasp under ambient conditions. Samples from the Base Metal As-Cast (AC) and Stir Zone (SZ) were microstructurally investigated before and after filing including the alloy in as cast state. The results showed that before filing SZ and AC samples presented equiaxial grains with the SZ sample having a much finer microstructure compared to AC. The values of grain sizes are around 150  $\mu\text{m}$  and 1-2  $\mu\text{m}$  for the AC and SZ samples, respectively. After filing, both samples presented similar grain sizes of only 60 nm. Although they attained similar grain sizes, the filings from SZ was more homogeneous and thinner the innerlayers, than its AC counterpart. The filings taken out from the SZ presented a much faster kinetics for hydrogen absorption mainly due to its homogeneous, thinner the innerlayers and its finer second-phase particle distribution, reaching up to 4.5 wt.% of hydrogen uptake against only 1.0 wt.% for AC sample after 10 hours of absorption in the first cycle. Both samples presented similar behavior for full discharge time. These results show the possibility of using FSP with subsequent filing as a mean to obtain materials with suitable properties for use as energy carriers with enhanced kinetics and better oxidation resistance in shorter processing times.

**ID-97****To the question of creation of the lithium cluster in Kazakhstan***D. Zhumabayeva*

This article discussed the possibility of the development of lithium cluster in the Republic of Kazakhstan. The materials of the lithium market and supply of raw lithium.

Determined the world market and the demand of lithium producers. The possibility of use lithium deposits. Li has been the implementation of the cluster of high-tech project in the Republic of Kazakhstan. Obtaining high purity lithium carbonate (battery grade) from spodumene are showed. The main deposits of lithium with geological characteristics of East Kazakhstan are considered.

ID-101

## Correlation between microstructure and hydrogen storage in Mg-based nanocomposites processed by high-pressure torsion

*M. Gajdics<sup>1</sup>, T. Spassov, V. Kovács Kis, E. Schafler, Á. Révész*

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Magnesium is considered as one of the most attractive hydrogen storage materials, mainly because of its high storage capacity (7.6 wt.%), lightweight and low cost. However the high thermodynamic stability and high desorption temperature of  $\text{MgH}_2$ , moreover the slow kinetics of sorption reactions hinder its use in a wide range of applications. There are multiple ways to improve the hydrogen sorption properties of Mg, ball-milling and different severe plastic deformation (SPD) methods are shown to be effective techniques. Among the SPD methods high-pressure torsion (HPT) can yield the largest deformation and it can even destabilize the hydrogen storing material [1]. Beside of that catalysts and alloying elements are also often used.  $\text{Nb}_2\text{O}_5$  is known to be one of the most remarkable catalyst of hydrogen sorption of Mg, furthermore carbon nanotubes can significantly accelerate sorption kinetics of hydrogen storing materials [2].

In the present work ball-milling of Mg powder was carried out with addition of  $\text{Nb}_2\text{O}_5$  and carbon nanotubes using a SPEX 8000 Mixer Mill. The milled powder was then subjected to high-pressure torsion following compaction of the powder material. In order to investigate the effect of the different additives on the kinetics and the rate-limiting step of the absorption-desorption reactions, samples with only one type of additive were also prepared. The microstructure of the processed material is studied by X-ray powder diffraction and transmission electron microscopy (TEM). Structural parameters like average crystallite size and size distribution were determined using X-ray line profile analysis. The hydrogen sorption properties were investigated using a Sieverts' type apparatus. Morphology and structure of carbon nanotubes in the HPT processed sample is studied by TEM to better understand their role in enhancing the sorption properties. Correlation between the structure and hydrogen sorption capabilities was investigated.

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ID-147

**Co doped MoS<sub>2</sub> nanosheets as efficient electrocatalyst for the hydrogen evolution reaction***B. K. Nguyen<sup>1</sup>, A. Manzo Robledo<sup>2</sup>, J. R. Vargas Garcia<sup>1</sup>*<sup>1</sup> *Instituto Politecnico Nacional- Esiqie, Depto. Ing. en Metalurgia y Materiales*<sup>2</sup> *INstituto Politecnico Nacional- Esiqie, Depto. Ing. Quimica*

Design and synthesis of efficient non-Pt catalysts represent a challenge for reaching the scalable production of hydrogen through the electrochemical splitting of water. Herein, the high electrocatalytic activity toward hydrogen evolution reaction (HER) of nanostructured Co-doped MoS<sub>2</sub> is demonstrated. It was found that small amounts of Co dopant improved significantly the electrocatalytic activity toward HER. Electrochemical measurements revealed that Co-doped MoS<sub>2</sub> exhibited highly attractive HER activity with a Tafel slope of 74 mV/decade besides high stability (negligible decrease of current density after 1000 cycles). These results proved the favorable effect of Co-doping in MoS<sub>2</sub> for water splitting.

ID-166

**Synthesis and characterization of one-dimensional MoO<sub>3</sub>-MoS<sub>2</sub>/C structures***A. R. Aguilera<sup>1</sup>, A. Verdejo Palacios<sup>1</sup>, J. R. Vargas García<sup>1</sup>**<sup>1</sup> Instituto Politécnico Nacional - Esiqie, Depto. Ing. Metalurgia y Materiales*

In this study we report the formation of one-dimensional MoO<sub>3</sub>-MoS<sub>2</sub>/C structures via sulfurization of multi-walled carbon nanotubes (MWCNTs) and subsequent Mo incorporation. The MWCNTs were first functionalized in nitric acid (40% v/v) under reflux at 90 - 100°C for 24 h. Sulfurization of functionalized MWCNTs was performed at room temperature by using CS<sub>2</sub> as S precursor. Mo was incorporated into the structure of the resultant sulfurized MWCNTs by a thermal decomposition method in vapor phase at 400°C using Mo(CO)<sub>6</sub> as Mo precursor. The incorporation of S and Mo atoms modify the structure of functionalized MWCNTs leading to the formation of crystalline MoO<sub>3</sub> and MoS<sub>2</sub> phases. The multiwalled structure of pristine carbon nanotubes was partially preserved, however, MoS<sub>2</sub> fullerene-like formations were observed inside the one-dimensional morphology. A decrease in diameter of the pristine nanotubes was observed due to the distortion of their crystal lattice by the substitution of carbon atoms. These results open the possibility of using a new and simple route in the vapor phase to obtain one-dimensional MoO<sub>3</sub>-MoS<sub>2</sub>/C structures, which are highly promising in electrocatalysis for hydrogen evolution.



ID-242

## Radio frequency sputtering deposition of iron oxide thin films for photoelectrochemical water splitting

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Photo-assisted processes are widely recognized as eco-friendly technologies in the field of renewable energy generation. In particular, a great effort is currently devoted to the development of technologies and materials suitable for the conversion of sunlight into chemical energy by photoelectrochemical water splitting. Iron(III) oxide in crystalline structure of hematite ( $\alpha\text{-Fe}_2\text{O}_3$ ) is considered a promising candidate as photoanode, thanks to its gap of 1.9-2.2 eV, allowing visible light absorption below 650 nm, large earth-abundance, low cost, non-toxicity, along with the stability in water and under illumination.

In this work, the RF sputtering deposition of iron oxides thin films in Ar/O<sub>2</sub> mixtures (O<sub>2</sub> = 0-50 %) is addressed. Film properties and photoelectrochemical activity are investigated as a function of oxygen percent in the gas feed mixture and of temperature during thermal annealing. A complete chemical (X-ray Photoelectron Spectroscopy, Fourier Transformed-Infrared spectroscopy), structural (X-ray diffraction, Transmission Electron Microscopy), morphological (field emission scanning electron microscopy), optical (UV-VIS spectroscopy) and photoelectrochemical characterization was performed. Results show that thin films deposited from an iron target in pure argon consist of metallic iron with an oxidized topmost layer, which can be turned into hematite by thermal annealing. In contrast, when oxygen was added to the feed mixture, hematite coatings were directly obtained from the deposition process. Film morphology is dominated by the presence of pyramidal aggregates with maximum dimension of 20 nm, when depositing in pure argon. A substantial modification occurs upon annealing with the formation of a network of elongated structures, giving rise to a porous film. A different morphology was observed for the coating obtained at 50% of oxygen percentage in the feed mixture, which was characterized by quasi-spherical structures with diameter up to 50 nm, uniformly distributed across the surface. Thermal treatment did not result in any substantial morphological variation, apart from a slight increase in surface roughness. Finally, photoelectrochemical characterization reveals that films obtained in pure argon are photoactive only after the thermal annealing, whereas the photoanode deposited at high oxygen concentration showed some photoactivity even before thermal annealing. The latter is in any case essential to significantly improve film performances.

ID-299

**Magnetic and magnetocaloric properties in Gd<sub>2</sub>O<sub>3</sub> electrospun nanofibers**A. M. Grishin<sup>1</sup>, N. P. Markova<sup>2</sup>, P. D. H. Yen<sup>3</sup>, S. C. Yu<sup>3</sup>, S. K. Oh<sup>3</sup>, T. D. Thanh<sup>4</sup><sup>1</sup>KTH Royal Institute of Technology<sup>2</sup>Petrozavodsk State University<sup>3</sup>Chungbuk National University<sup>4</sup>Institute of Material Sciences, VAST

Recently, gadolinium based compounds showed promising properties with a large magnetocaloric effect (MCE). Being a pure paramagnetic material, gadolinium oxide demonstrated strong MCE in nanosized Gd<sub>2</sub>O<sub>3</sub> crystals. Isolated Gd<sub>2</sub>O<sub>3</sub> nanoparticles with a diameter of 6-8 nm embedded in a mesoporous silica matrix showed the entropy change  $S_{\max} \sim 40$  J/kgK at 3 K with magnetic field change of 5 T that was ascribed to a second transition phase from paramagnetic to spin glass-like state [1]. Anisotropic MCE was observed in crystalline Gd<sub>2</sub>O<sub>3</sub> nanotubes though the maximum achieved  $S_{\max}$  did not exceed 16 J/kgK at 7 T of magnetic field change. The presence of superparamagnetic clusters in Gd<sub>2</sub>O<sub>3</sub> nanotubes was confirmed and said to be caused by the aggregation of Gd<sub>2</sub>O<sub>3</sub> nanoparticles on surface of nanotubes [2].

In this work, the magnetic and magnetocaloric properties of crystalline Gd<sub>2</sub>O<sub>3</sub> nanofibers are presented. The large length-to-diameter aspect ratio nanofibers synthesized by electrospinning method showed a single phase in C-type cubic structure [3]. Gd<sub>2</sub>O<sub>3</sub> fibers show superparamagnetic behavior and high 1/T<sub>1</sub> and 1/T<sub>2</sub> proton NMR relaxivities were observed in Gd<sub>2</sub>O<sub>3</sub> fibers capped with diethyleneglycol (DEG). A small difference in temperature range below 200 K of FC/ZFC curves at 100 Oe of applied magnetic field and a small deviation from Curie-Weiss behavior of inverse susceptibility with negative  $\theta$  value confirmed the weak superparamagnetic state. Magnetocaloric properties of Gd<sub>2</sub>O<sub>3</sub> nanofibers were evaluated from indirect measurements of isothermal magnetization M(H) data. At 5 K pure Gd<sub>2</sub>O<sub>3</sub> nanofibers fabric exhibits the entropy change as large as 28 J/kgK at magnetic field variation of 7 T. Strong MCE exhibits crystalline Gd<sub>2</sub>O<sub>3</sub> nanofibers as a prospective refrigerating agent for micro- and nano-electromechanical systems.

ID-315

**Binder-free Cellulose-derived Carbon/SnO<sub>2</sub> electrospun nanofibers as long-life Li-Ion battery electrodes***S. Oh, J. Kim, D. Kim*

Bio-inspired carbon materials have been attracted as anodes in lithium ion battery applications because of their excellent electrical conductivity and cycling retention. Among them, cellulose-based carbon anodes are widely studied in many fields due to its many advantages such as environmental friendly, low cost, and the most abundant renewable resource on the earth. However, carbon-based anode materials have relatively low energy density and poor specific capacity. To improve the specific capacity, cellulose-based carbon and Li-alloying material (Si, Sn, Sb, Ge) composites are considered as promising anode materials owing to low cost and their high theoretical capacity. Nevertheless, Li-alloying material's intrinsic drawback of high volume expansion is still remained.

To overcome volume change issue upon cycling, designing one-dimensional nanostructured materials is an effective way owing to its unique advantage of buffering volume expansion, efficient electron pathway, and large surface area. Many state-of-the-art research have been reported cellulose-based electrospun nanofibers using cellulose acetate (CA) and their good stability. In this study, we synthesized cellulose-based carbon nanofibers and SnO<sub>2</sub> composite nanofibers via single-nozzle electrospinning process using CA and SnO<sub>2</sub> nanoparticles. Firstly, 3 g of CA was dissolved in 12 mL acetone/dimethyl acetamide mixture solvent (1:1 = v/v). The CA solution was loaded on the electrospinning equipment and a high voltage of 16 kV were applied to metal needle with a flow rate of 0.5 mL/h. As-prepared CA nanofibers were deacetylated for 24 hours in 0.05 M NaOH solution to regenerate into cellulose. Finally, cellulose-based carbon nanofibers (CC NFs) were fabricated after carbonization process at 600°C for 2 hours in Ar. For improving electrochemical performance, the cellulose-based carbon and SnO<sub>2</sub> composite nanofibers were prepared using CA solution including commercial SnO<sub>2</sub> nanoparticles (< 100 nm, c-SnO<sub>2</sub>) or hydrothermally synthesized SnO<sub>2</sub> nanoparticles (≈ 10 nm, h-SnO<sub>2</sub>). The punched CC NFs, CC/c-SnO<sub>2</sub> NFs, and CC/h-SnO<sub>2</sub> NFs were evaluated directly in Li-ion battery tests without binder. CC/c-SnO<sub>2</sub> NFs and CC/h-SnO<sub>2</sub> NFs electrodes have much better specific capacities than CC NFs and the all electrodes show excellent stability over 400 cycles. This excellent electrochemical performance was attributed to one-dimensional bio-inspired cellulose carbon nanofibers with dispersion SnO<sub>2</sub> nanoparticles.

ID-316

**Synthesis and electrochemical investigation of  $\text{Zn}_{1.67}\text{Mn}_{1.33}\text{O}_4$  microspheres as a new anode material for Lithium Ion battery***J. W. Lee<sup>1</sup>, S. D. Seo<sup>1</sup>, D. W. Kim<sup>1</sup>*<sup>1</sup> Korea University

Rechargeable lithium ion batteries have been used as energy storages device for portable electronics, electric tools due to their high energy density, high rate capability and long-term stability. Nowadays, they continue to draw attention because their potential for applications in new fields, such as electric vehicles, electrochemical energy storage systems. [1] Transition metal-based oxides (TMOs) are one of attractive anode materials because the acceptable lithiation potentials and their high theoretical capacities owing to the conversion reaction with lithium. Among the TMOs, zinc manganese oxide has many advantages, such as low cost, environmental benignity, and lower operating voltage in comparison with Co or Fe based oxides. [2]

In this study, we firstly reported the synthesis of the  $\text{Zn}_{1.67}\text{Mn}_{1.33}\text{O}_4$  (ZMO) microspheres, which have the aggregated morphology of nanoparticles, and its electrochemical performance with lithium. ZMO was synthesized by simple hydrothermal route. The ethylene glycol and deionized water used as solvent and molar ratio-controlled zinc/manganese acetate also used as metal source to obtain a specific phase. Furthermore, the ammonium bicarbonate and urea also added to obtain an aggregated morphology with some porosity. After the synthetic process, the collected  $\text{Zn}_x\text{Mn}_{1-x}\text{CO}_3$  microspheres were calcined to ZMO at 600°C, air atmosphere. The electrochemical properties of ZMO electrode were investigated using Swagelok-type half-cell with lithium as a counter. In typical TMO do only the conversion reaction, ZMO shows extra alloying reaction by the existence of Zn, which provides the additional specific capacity. ZMO exhibits high 1<sup>st</sup> discharge/charge capacity of 1171 mA h g<sup>-1</sup> and 768 mA h g<sup>-1</sup>, respectively. After 20 cycles, it shows 683 mA h g<sup>-1</sup>. Furthermore, the ZMO microspheres were composited with graphene nanosheets to improve the cycle performance by the enhanced electrical conductivity.

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ID-327

**Comparison of graphene hybridized CeO<sub>2</sub> nanoparticles and nanorods for Lithium-Air battery cathodes***M. C. Sung, G. H. Lee, D. W. Kim*

CeO<sub>2</sub> have been broadly applied as a promising semiconductor for fuel cells, ultra-violet absorbents, oxygen gas sensors due to low cost, high redox property, fast oxygen transportability, and non-toxicity. Additionally, CeO<sub>2</sub> has been extensively studied as an accelerator for many catalyst systems owing to the existence of Ce<sup>4+</sup>/Ce<sup>3+</sup> redox pair. The multivalence property of CeO<sub>2</sub> will offer the opportunity to generate strong electron interactions with other matrices that can improve catalytic performance. This key candidate material with unique properties is an excellent catalyst applied in lithium–air batteries. Additionally, the catalytic activity of CeO<sub>2</sub> nanostructures is strongly dependent on their surface structure/chemistry, so various nanoparticles, nanorods, and nanotubes have been successfully synthesized by chemical methods.

In this study, we synthesized CeO<sub>2</sub> nanoparticles and nanoparticles/nanorods hybrid nanostructure by facile hydrothermal process without any template and surfactant. As per the typical procedure, The Ce(NO<sub>3</sub>)<sub>3</sub> aqueous solution was adjusted to 10.25 by the addition of NH<sub>4</sub>OH. The autoclave was heated at 90 °C for 0 or 60 min, respectively. The as-synthesized CeO<sub>2</sub> nanoparticles exhibit single crystalline with a diameter of < 10 nm and the CeO<sub>2</sub> nanorods exhibit 1D morphology with width of ~10 nm. We suggest that the conversion from nanoparticles to nanorods involved a dissolution-recrystallization process under the strong basic hydrothermal condition. For initial reaction, CeO<sub>2</sub> crystals were preferred to form hexagonal nanoparticles. As the reaction time increases, CeO<sub>2</sub> crystals tune the surface free energies thus induce the growth rates of different facets, leading to the formation of CeO<sub>2</sub> nanorods. Using lithium–air cells, we discuss their electrocatalytic activities of CeO<sub>2</sub> samples through the series of the electrochemical rechargeability by the oxygen reduction and evolution kinetics such as cyclic voltammetry, galvanostatic cycling. Moreover, with the aid of small amount of graphene acting as conductive support, graphene/CeO<sub>2</sub> hybrid nanostructures were also prepared in order to improve electrocatalytic activities. Compared to pure CeO<sub>2</sub>, graphene/CeO<sub>2</sub> hybrid nanostructures exhibit low overpotential characteristics and cyclic stability due to enhanced electrical conductivity. We performed electrochemical impedance spectroscopy analysis to determine the relationship between the electrochemical performance and electrode kinetics.

ID-343

**Zn-based semiconductor nanopowders doped by mechanical milling**L. G. Valluzzi<sup>1</sup>, M. G. Valluzzi<sup>1</sup>, L. C. Damonte<sup>2</sup>, M. Meyer<sup>2</sup><sup>1</sup> IDEI, Universidad Nacional de Tierra del Fuego (UNTDF)<sup>2</sup> Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata (UNLP), CC 67, 1900 La Plata, Argentina - Instituto de Física La Plata (IFLP, CONICET), La Plata, Argentina

II-VI semiconductors are of interest due to their potential application as photo-voltaic devices like hybrid solar cells. The efficiency of these devices may be improved mainly increasing charge carriers densities and interfacial processes. In order to reach this last purpose nanocrystalline materials are the best option as solar cells constituents. In this study we present zinc based semiconductors powders which optical and electrical properties have been modified by the Al presence acting as small quantities of dopant.

The nanosized doped semiconductors (ZnO, ZnSe and ZnTe) were obtained by mechanical milling which has been proved to be an effective and simple technique to produce nanocrystalline and large quantities of materials. The starting materials, the metal oxides ( $Al_2O_3$ ) or the pure metal (Al) together with ZnO, ZnSe or ZnTe were milled in adequate proportion to obtain the desired concentration. Parameters such as initial concentrations, atmosphere and milling times were varied. Structural and optical characterization of doped powders by X-ray diffraction, Extended X-ray Absorption Spectroscopy (XAFS), scanning electron microscopy, positron lifetime measurements (PALS) and optical reflection spectroscopy were done. Undoped ZnO, ZnSe and ZnTe nanocrystalline powders prepared in a similar way were analyze for comparison. The knowledge obtained can be of use to give direction to the improvement of the performance of hybrid organic/inorganic solar cells.

ID-366

**Evaluation of the magnetocaloric effect in polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$  ( $x=0, 0.02, 0.07, 0.1$ ) samples synthesized by ball milling***A. Gómez<sup>1</sup>, O. Morán<sup>1</sup>, J.S. Blázquez<sup>2</sup>, A. Conde<sup>2</sup>, J.J. Ipus<sup>2</sup>, V. Franco<sup>2</sup>, N. Rojas<sup>3</sup>, J.L. Izquierdo<sup>4</sup>*<sup>1</sup> *Universidad Nacional de Colombia*<sup>2</sup> *Universidad de Sevilla*<sup>3</sup> *Centro de Investigación en Metalurgia Extractiva (CIMEX)*<sup>4</sup> *Centro de Investigación y Desarrollo en Metalografía*

The effect of the vial frequency and the milling time on the structural, magnetic and magnetocaloric properties of polycrystalline  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$  ( $x=0, 0.02, 0.07, 0.1$ ) samples is reported. The mechano-chemical process was performed at room temperature in a Fritsch Pulverisette 4 Vario- Planetary Mill using hardened steel balls and stainless steel vials in air atmosphere. The ball to powder weight ratio was 10:1 and the main disk frequency was set to 250 and 350 rpm (frequency ratio vial to main disk -2). X-ray diffraction analysis indicated that a single  $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (LCMO) phase was completely formed at 350 rpm after 155 h of milling. The amount of LCMO phase grows exponentially with milling time. Furthermore, the increase in milling time leads to a decrease in crystal size. The equivalent time approach is confirmed for the synthesis of this kind of manganite in an equivalent amount after 25.5 h at 350 rpm or 70 h at 250 rpm. The dependence of the magnetization on the temperature revealed a well-defined paramagnetic-ferromagnetic transition for all the compositions. Interestingly, the values of the Curie temperature shifted to higher values for  $\text{Ni}^{2+}$  doping levels  $x=0.07$ . Arrott plots showed that the nature of the magnetic phase transition is second order. The maximum magnetic entropy changes observed for  $x=0, 0.02, 0.07, 0.1$  compounds are 1.16, 0.69, 0.60 and 0.78 J/kgK, respectively, under a magnetic field of 1.5 T. The obtained results show that high-quality  $\text{La}_{0.7}\text{Ca}_{0.3}\text{Mn}_{1-x}\text{Ni}_x\text{O}_3$  samples can be obtained by mechano-synthesis.

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ID-370

**Magnetocaloric properties of FeNiGaMnSi high entropy alloys***K. Sarlar<sup>1</sup>, I. Kucuk<sup>1</sup>*<sup>1</sup> *Uludag University*

High entropy alloys (HEAs) have begun to attract more attention from researchers with their unique structures and excellent properties such as high strength, good wear resistance, corrosion resistance, soft magnetic properties and thermal stability. In the present study, FeNiGaMnSi high entropy alloy rods with a diameter of 2mm were prepared by arc-melting and suction casting. The structures of samples were identified by X-ray diffraction (XRD) with  $\text{CuK}\alpha$  radiation. The magnetic properties measurements were conducted with a Microsense EZ9 vibrating sample magnetometer (VSM). The temperature dependence of magnetisation (M-T) curves from 200 K to 500 K were measured under a field of 0.01 T and the isothermal initial magnetisation curves (M-H) were measured under a field of 0–2 T. This high entropy alloys show large magnetocaloric effect and refrigeration capacity at low field reported so far. This unique property makes the FeNiGaMnSi high entropy alloy promising for magnetic refrigeration applications.



ID-438

**Magnetic properties of exchange coupled nanocomposites obtained by milling  $\alpha$ -Fe and recycled  $\text{SmCo}_5$** *A. Chakraborty<sup>1</sup>, R. Hirian<sup>2</sup>, I. Škulj<sup>3</sup>, V. Pop<sup>4</sup>*<sup>1</sup> MAGNETI Ljubljana d.d.<sup>2</sup> Babes-Bolyai University - Faculty of Physics<sup>3</sup> R&D, MAGNETI Ljubljana d.d.<sup>4</sup> Faculty of Physics, Babeş-Bolyai University

Permanent magnets {PM} are a driver of modern technology and are crucial to industry. A property of interest in PM is the energy product  $\{(BH)_{\max}\}$  – determining the work extractable from a given magnet volume [1]. Improving PM efficiency means maximizing  $(BH)_{\max}$  while using less materials, which also leads to miniaturization.

Modern PM are intermetallic alloys that contain appreciable amounts of lanthanide elements along-side iron {Fe} and cobalt. Excepting Fe, the other elements come from minerals mined in regions of conflict, or are susceptible to geopolitical control via embargos, with high environmental and human cost [2]. Our goal is to make PM that minimize dependence on such critical minerals while still providing high-performance.

Exchange spring magnets {SPM} consist of hard and soft magnetic materials in a diffuse nano-scale composite. In SPM, exchange-coupling between neighbouring soft/hard crystallites can improve  $(BH)_{\max}$  when the structure, microstructure, and geometry meet certain criteria [3]. We aim to create functional nanocomposite exchange-coupled PM that use recycled materials. Use of recycled materials can minimize the footprint and environmental costs of critical elements; this is in addition to savings accrued by the advantages of SPM alone – such improvement constitutes the plinth of our project. [4]

This study uses 10% Fe as the soft-magnetic phase fraction and 90% Samarium-Cobalt 1:5  $\{\text{SmCo}_5\}$  as the hard-magnetic phase. Our material choice is dictated by the naturally high moment available in Fe and the high anisotropy of  $\text{SmCo}_5$  [1]. We select high-energy ball-milling to create a homogenous powder which is further annealed specifically to relax structural stress, improve the crystallinity of the hard magnetic phase, while also minimizing Fe grain-growth.

X-Ray diffraction shows the average Fe crystallite sizes are under 20 nm. Hysteresis measurement (room-temperature, 10 T) of powders annealed above and below iron recrystallization temperatures show remanence up to 70 Am<sup>2</sup>/kg, coercivities above 1.5 T, and high remanence ratios. Further work will be towards consolidating the powder to form bulk SPM, aiming for high  $(BH)_{\max}$  values.

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ID-483

**Synthesis of new thiospinel  $\text{MgCr}_2\text{S}_4$  for multivalent battery cathode applications***L. Caggiu<sup>1</sup>, G. Mulas<sup>2</sup>, S. Enzo<sup>2</sup>, S. Garroni<sup>3</sup>, L. Stievano<sup>4</sup>, R. Berthelot<sup>4</sup>*<sup>1</sup> *Università degli Studi di Sassari*<sup>2</sup> *University of Sassari, Department of Chemistry and Pharmacy*<sup>3</sup> *University of Burgos*<sup>4</sup> *Université Montpellier*

The ever increasing demand for energy storage is currently focusing for making available electricity based on new battery systems [1,2]. A range of new compounds that could have excellent electrochemical properties (good mobility and acceptable voltage) have been considered recently by Liu et al.[3] using a DFT computational approach. After optimization of the “Energy Above Hull”[3], the  $\text{MgCr}_2\text{S}_4$  compound was suggested to be an interesting candidate as multivalent battery cathode. Unfortunately from the synthetic chemistry approach, such thiospinel turns out to be of difficult control in the right stoichiometric proportion. On the other hand, the well-known potential of Mechanical Alloying to overcome the strong physical limitations of immiscibility[4,5] between magnesium and chromium in their equilibrium phase diagram, has stimulated our attempts for a solid state synthesis route starting from magnesium or magnesium hydride, chromium and sulphur powders. The course of such mechanically induced reaction as a function of processing time was checked intermittently by XRD and it was evidenced the occurrence of a discontinuous event suggesting a mechanically induced self-propagating reaction, MSR. After inspecting the energetic parameters associated to the milling apparatus, (e.g., frequency of vibrating media, ball-to-powder ratio, stoichiometry, etc.), the analysis of the reaction products shows that  $\text{MgCr}_2\text{S}_4$  (space group  $fd-3m$ ,  $a=10,137 \text{ \AA}$ ) partially occurs. Results will be presented in order to drive the kinetics and to maximize the amount of such phase.

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ID-486

**Characterization of alloys  $\text{TiCr}_{1.1}\text{V}_{0.9}$ ,  $\text{TiCr}_{1.2}\text{V}_{0.8}$ ,  $\text{TiCr}_{1.3}\text{V}_{0.7}$  obtained by mechanical alloy for storage of hydrogen in the solid state***A. Martínez<sup>1</sup>, D. Peña<sup>2</sup>, D. Pacheco<sup>2</sup>, J. Correa<sup>2</sup>*<sup>1</sup> *Universidad de Santander, Grupo de Nuevas Tecnologías, Colombia*<sup>2</sup> *Universidad Industrial de Santander, Grupo de Investigación en Corrosión, Colombia*

At present, a high percentage of the world's energy demand is covered by fossil fuels such as coal, oil and natural gas. However, fossil fuels are non-renewable energy resources and it is estimated that in the coming decades there will be a significant decrease in their availability and production. On the other hand, the combustion of fossil fuels gives rise to the emission of  $\text{CO}_2$ , which is the vital responsible for global warming and climate changes related to our planet. Hydrogen is considered a promising candidate as an energy vector due to its clean combustion (generates water as a byproduct) and high calorific value, 572 kJ/mol, approximately three times that of gasoline. Naturally the  $\text{H}_2$  is in minimum quantities, therefore, it would have to be produced, for example, from the dissociation of water by means of electrolysis. One of the keys is its storage, which can be through pressurized tanks, at low temperatures such as the use of cryogenic techniques to store it in the most promising liquid state, the metal hydrides. In this research work is studied the behavior in terms of hydrogen storage capacity of three alloys;  $\text{TiCr}_{1.1}\text{V}_{0.9}$ ,  $\text{TiCr}_{1.2}\text{V}_{0.8}$ ,  $\text{TiCr}_{1.3}\text{V}_{0.7}$  which were synthesized by mechanical grinding for the absorption capacity a Sieverts type device is used, for the superficial study an XPS is developed, for the morphology it is used SEM and for the measurement of the network parameters X-rays are used. In the first tests large storage capacity of the order of 3.5 wt% at room temperature is observed and pressures of 10 bar the capacity decreases when the amount of Vanadium is decreased.

ID-491

**NiCo alloys as catalyst for magnetically induced dry reforming of methane***F. Varsano<sup>1</sup>, M. Bellusci<sup>1</sup>, F. Padella<sup>1</sup>, A. La Barbera<sup>1</sup>, M. Albino<sup>2</sup>, M. Petrecca<sup>2</sup>, D. Peddis<sup>3</sup>, C. Sangregorio<sup>2,4</sup>*<sup>1</sup> ENEA - C.R. Casaccia, Via Anguillarese 301, 00123 Roma, Italy<sup>2</sup> INSTM and Dip di Chimica, Università di Firenze, via della Lastruccia 3, 50019, Sesto F.no, Italy<sup>3</sup> ISM-CNR, Roma, Monterotondo Scalo (RM), Italy<sup>4</sup> ICCOM- CNR, via Madonna del Piano 10, 50019 Sesto F.no, Italy

The possibility of converting electromagnetic energy into heat utilizing magnetic materials has been recently exploited to satisfy the energetic needs of chemical processes [1, 2]. Energy is supplied by a radiofrequency alternating magnetic field in a fast and efficient way to a properly responding catalytic system, generally containing both a magnetic and a catalytic component. In such a way heat is provided directly by the catalytic bed avoiding unnecessary heating (and dissipation) of the whole chemical reactor, lay down the premises for “cold catalysis”.

Here we report the activation of the dry reforming reaction by induction heating by means of a NiCo alloy. The catalyst plays a double role, serving both as a promoter for the reforming reaction and heat generator by dissipation of the electromagnetic energy. The elevated temperatures imposed by the reforming reaction require the choice of an alloy with a Curie temperature  $>800^{\circ}\text{C}$  a condition which is fulfilled by NiCo alloy with a 60:40 weight ratio, the catalyst used in this work. NiCo alloy has been synthesized by arc melting starting from metal pellets and catalytic sites for  $\text{CH}_4$  and  $\text{CO}_2$  activation are created by a mechanochemical treatment that increases solid-state defects. The catalyst powder has been pressed into cylindrical pellets and successively tested in a continuous-flow reactor working under atmospheric pressure. Methane conversion and hydrogen production yields have been measured as a function of the applied magnetic field, reactant flow rate and time on stream. Methane conversion values of 95% have been observed utilizing a 300 mg single pellet operating at 22 mT and 190 kHz, atmospheric pressure, gas hourly space velocity of  $2.5 \cdot 10^{4\text{h}^{-1}}$ .

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[2] A. Bordet, L-M. Lacroix, P-F. Fazzini, J. Carrey, K. Soulantica, B. Chaudret, Magnetically induced continuous  $\text{CO}_2$  hydrogenation using composite iron carbide nanoparticles of exceptionally high heating power, *Angew. Chem. Int. Ed.* 2016, 55, 15894-15898.

**Wednesday 4 July afternoon - 17:30/18:30**

Poster Session 3

**MAGNETIC, TRANSPORT AND OPTICAL PROPERTIES FROM  
NANOSCALE TO BULK**

Chair: G. Muscas and G. Barrera

ID-153

**Thermodynamic modeling of formation enthalpy, structural and magnetocaloric properties of half-Heusler (Mn,X)-Co-Ge (X = Zr, Pd) alloys***P. Gebara*<sup>1</sup>, *Z. Śniadecki*<sup>2</sup><sup>1</sup>*Institute of Physics, Czestochowa University of Technology, Armii Krajowej 19 Av., 42-200 Czestochowa, Poland*<sup>2</sup>*Institute of Molecular Physics, Polish Academy of Sciences*

In the present work, the semi-empirical Miedema's model combined with the geometric one were used to determine enthalpy of formation of half-Heusler Mn-Co-Ge alloys, where partial substitution of Mn by Zr or Pd was applied. Enthalpies of formation of different structural states were determined and discussed in relation to experiment. Samples were obtained by arc-melting of high purity elements under low pressure of Ar atmosphere. Phase constitution was studied using Bruker D8 Advance equipped with semiconductor Lynx Eye detector. Thermomagnetic curves and magnetic isotherms were measured using Quantum Design PPMS (VSM option) in wide temperature range and in magnetic field of up to 5T. These measurements allowed to reveal the Curie temperature  $T_C$  and a magnetic entropy change  $\Delta S_M$ . The XRD studies confirm the presence of orthorhombic structure for parent MnCoGe alloy. In the case of Zr substituted sample, two orthorhombic structures with different lattice constants were identified. Similar results were observed in the specimen modified by Pd. The Curie temperatures are equal to 293, 278 and 318K for MnCoGe,  $Mn_{0.9}Zr_{0.1}CoGe$  and  $Mn_{0.9}Zr_{0.1}CoGe$ , respectively. The maximum magnetic entropy change  $\Delta S_M$  values, calculated for the change of external magnetic field of  $\sim 5$  T, amount to 6.17, 2.94, 11.11 J/(kg K) for MnCoGe,  $Mn_{0.9}Zr_{0.1}CoGe$  and  $Mn_{0.9}Zr_{0.1}CoGe$ , respectively.

ID-181

**Magnetic properties, thermal stability and crystallization study of high induction metallic ribbons  $\text{Fe}_{67}\text{Co}_{20}\text{B}_{13}$** 

*P. Zackiewicz<sup>1</sup>, L. Hawelek<sup>1</sup>, P. Włodarczyk<sup>1</sup>, J. Ferenc<sup>2</sup>, M. Kowalczyk<sup>2</sup>, M. Polak<sup>1</sup>, M. Karpinski<sup>1</sup>, M. S. Kempka<sup>1</sup>, A. K. Burian<sup>1</sup>*

<sup>1</sup> *Department of Functional Materials, Institute of Non-Ferrous Metals*

<sup>2</sup> *Faculty of Materials Science and Engineering, Warsaw University of Technology*

The high induction metallic glass ribbons obtained via melt spinning technique with the chemical formula  $\text{Fe}_{67}\text{Co}_{20}\text{B}_{13}$  were investigated in order to study their thermal stability, crystallization and magnetic properties like complex permeability, magnetic saturation and coercivity. Thermal properties: solidus-liquidus curves of the master alloy, the crystallization temperatures and kinetics of the crystallization process of the ribbons were analysed by applying differential scanning calorimetry. The crystal structure of the prepared ribbons as well as kinetics of the isothermal crystallization were examined by X-ray diffraction method. Ribbons were annealed both conventionally as toroidal cores in high temperature vacuum furnace and as ribbon pieces in rapid annealing process between two preheated iron blocks. The comparison of these two processes allows us to find optimal heat treatment to achieve best possible magnetic properties for this type of material.

ID-232

## Structure and magnetic behavior of Ni-Mn based Heusler alloys produced by ball milling

S. Joan<sup>1</sup>, L. Escoda<sup>2</sup>, G. J.M.<sup>1</sup>, L. Nuria<sup>3</sup>, R. Antoni<sup>3</sup>, J. J. Suñol<sup>2</sup>

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<sup>3</sup> Universitat de Barcelona

Some Heusler Ni-Mn-(Sn,In) alloys are characterized by both structural transformation (from austenite to martensite) and magnetic (usually from paramagnetism to ferromagnetism) transformation when the temperature decreases. These alloys can be produced in bulk, ribbon, microwire or powder shape. Normally, the dimensional reduction involves the reduction of the temperatures of the structural transformation, or even its inhibition. In this work, several nanostructured alloys of the Ni-Mn-(Sn, In) system have been produced in powder form and characterized. The production has been carried out in three stages: bulk alloys formation by means of arc-melting, ribbons production by melt-spinning and finally, powders by ball milling of ribbon flakes. The size reduction of the ribbons was checked using a 50 m sieve to control the percentage of original ribbon considered as well fractured or powdered-like. The sample thermal characterization was carried out by differential scanning calorimetry (DSC), the morphology and composition study was performed by scanning electron microscopy (SEM) coupled with energy dispersive X-ray microanalysis (EDX), the crystallographic analysis with X-ray diffraction (XRD) and the magnetic properties by vibrating sample magnetometry (VSM). As milled nanocrystalline powder samples usually show a clear decrease in the magnetic and thermomagnetic response (around 40 - 50%) with respect to the ribbons. In some cases, even the structural transformation is not detected. The XRD measurements show a significant increase of the crystallographic defects induced by milling and even the destruction of the crystalline structure. In order to recover values comparable to those of ribbons [1], it is necessary to carry out adequate thermal treatments. Not all annealing implies a significant improvement of the magnetic and thermomagnetic response of the samples. Likewise, magnetic analysis confirms both structural and magnetic transformations with a shift in temperatures due to applied magnetic field.

[1] K. Dadda, S. Alleg, S. Souilah, J.J. Suñol, E. Dhahri; L. Bessais, E.K. Hlil. Journal of Alloys and Compounds 735, 1662- 1672 (2018)

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ID-251

**The effect of stress-annealing on magnetic properties of thick microwires***P. Corte-Leon<sup>1</sup>, V. Zhukova<sup>1</sup>, M. Ipatov<sup>1</sup>, J. M. Blanco<sup>2</sup>, J. Gonzalez<sup>1</sup>, A. Zhukov<sup>1</sup>*<sup>1</sup>*Dept. Phys. Mater., University of Basque Country, UPV/EHU San Sebastián 20018, Spain*<sup>2</sup>*Dpto. de Física Aplicada, EUPDS, UPV/EHU, 20018, San Sebastian, Spain*

Amorphous and nanocrystalline alloys attracted considerable attention mostly owing to excellent soft magnetic properties [1]. Among these materials, amorphous wires exhibiting several outstanding features, such as giant magneto-impedance, GMI effect, spontaneous magnetic bistability and fast domain wall dynamics gained certain interest [1]. Amorphous wires produced by so-called “in rotating water” technique with diameter of 120  $\mu\text{m}$  have been introduced in 80-th [1]. Particularly, it was found that ferromagnetic amorphous wires exhibit spontaneous magnetic bistability for composition with positive or negative magnetostriction constant [1]. At the same time, soft magnetic properties and GMI effect have been observed for low-magnetostrictive compositions [1].

The alternative (Taylor-Ulitovsky) technique allowing preparation of glass-coated microwires (typical metallic nucleus diameters of 0.5–40  $\mu\text{m}$ ) is known since 60-s [2]. In spite of elevated magnetoelastic anisotropy [3], glass-coated microwires provide a number of advantages, such as flexible, bio-compatible and insulating glass-coating, extremely high GMI ratio (up to 600%), and very fast (with velocities up to 2–3 km/s) single DW propagation [3]. Although generally thinner wires present certain advantages related to industrial application, for some applications (like non-contact stress monitoring or magnetic tags) thicker wires are needed. However, it is generally considered that Taylor-Ulitovsky technique is restricted to preparation of thin magnetic wires.

We studied the as-prepared and annealed Fe<sub>71.7</sub>B<sub>13.4</sub>Si<sub>11</sub>Nb<sub>3</sub>Ni<sub>0.9</sub> glass coated microwire with metallic nucleus diameter  $d = 103 \mu\text{m}$  and total diameter  $D = 158 \mu\text{m}$  prepared by Taylor-Ulitovsky method described elsewhere [3]. Amorphous structure of as-prepared wires is confirmed by X-ray diffraction.

As-prepared glass-coated wires present relatively low GMI effect (GMI ratio,  $\Delta Z/Z \approx 50\%$  at 500 MHz) and relatively low coercivity (about 25 A/m). After stress-annealing we observed considerable improvement of the GMI ratio (from 50% up to 130 % at 500 MHz).

Resuming, aforementioned studies allow us to obtain thick ferromagnetic wires with good magnetic properties and GMI effect suitable for industrial applications.

[1] K. Mohri et.al., IEEE Trans.Magn., Mag-26, 1789 (1990)

[2] R. Gemperle, et.al., Czech. J. Phys. B 28, 1138 (1978)

[3] A. Zhukov et.al., J. Alloys Compound. 727, 887 (2017)

ID-252

**Engineering of magnetic properties of Co- rich microwires by Post-processing**L. G. Legarreta<sup>1</sup>; V. Zhukova<sup>1</sup>; P. C. León<sup>1</sup>; M. Ipatov<sup>1</sup>; J. M. Blanco<sup>2</sup>; A. Zhukov<sup>1</sup><sup>1</sup>Dept. Phys. Mater., University of Basque Country, UPV/EHU San Sebastián 20018, Spain<sup>2</sup>Dpto. de Física Aplicada, EUPDS, UPV/EHU, 20018, San Sebastian, Spain

Thin magnetic wires exhibiting excellent magnetic softness combined with good mechanical properties are extremely demanded by developing industries [1,2]. Some magnetic properties of magnetic wires, such as single domain wall (DW) propagation or giant magnetoimpedance (GMI) effect are common features of crystalline and amorphous magnetic wires and intrinsically related to the cylindrical symmetry [1,2].

Additionally, glass-coated microwires provide a number of advantages, such as thinnest diameters, flexible, biocompatible and insulating glass-coating.

Recently, the induced magnetic bistability and fast DW propagation have been reported in properly annealed Co-rich microwires [2]. An interesting feature of the annealed Co-rich microwires is that they also present an elevated GMI effect [2].

We present our last results on tailoring of magnetic properties and GMI effect of Co-rich glass-coated microwires by annealing.

We studied GMI effect and DW dynamics of Co-rich  $\text{Fe}_{3.61}\text{Co}_{69.22}\text{Ni}_{0.99}\text{B}_{12.28}\text{Si}_{10.73}\text{Mo}_{1.44}\text{C}_{1.19}$  glass-coated microwires (metallic nucleus diameter,  $d \approx 22.8\mu\text{m}$ ; total diameter  $D=23.2\mu\text{m}$ ). Similarly, to recently reported results for Co-rich microwires (i.e. in  $\text{Co}_{69.2}\text{Fe}_{4.1}\text{B}_{11.8}\text{Si}_{13.8}\text{C}_{1.1}$ ) we observed the considerable coercivity increase related to transformation of hysteresis loops from linear to rectangular in studied microwires after conventional annealing.

Despite that the stress-annealed microwires also present rectangular hysteresis loops, the  $H_c$  -values of the stress-annealed microwires are considerably lower than that annealed without stress. We also observed an increase of GMI effect in annealed and stress-annealed microwires as compared to as-prepared microwires. In all the annealed and stress-annealed samples presenting rectangular hysteresis loops we observed the remagnetization by single DW propagation. The DW velocity,  $v$ , and DW mobility,  $S$ , depend on annealing conditions. At certain annealing conditions we observed  $v$  up to 4 km/s and  $S$  up to 29 ( $\text{m}^2/\text{s}\cdot\text{A}$ ).

Observed change of hysteresis loop discussed considering the modification of the magnetostriction coefficient after annealing and modification of the domain structure (increase of the volume of the inner axially magnetized core radius) related to the stress relaxation and stress-induced magnetic anisotropy.

[1] K. Mohri et.al. IEEE Trans.Magn., Mag-26, 1789, (1990),

[2] A. Zhukov et.al. J. Alloys Compound. 727 887, (2017).

ID-253

**Facile batch-scale production of spinel ferrite for permanent magnet application**C. Galassi<sup>1</sup>, C. Innocenti<sup>2</sup>, C. Sangregorio<sup>3</sup>, M. Petrecca<sup>2</sup>, P. Galizia<sup>1</sup><sup>1</sup>CNR -ISTEC, Via Granarolo, no.64, I - 48018, Faenza, Italy<sup>2</sup>INSTM and Dept. of Chemistry "U. Schiff", Univ. of Florence, via della Lastruccia, no. 3, I-50019 Sesto Fiorentino, Italy<sup>3</sup>CNR-ICCOM, via Madonna del Piano no. 10, I-50019 Sesto Fiorentino, Italy

The rising demand for rare-earth elements to realize permanent magnets for renewable energy production and other industrial applications is pushing the search of new rare-earth free solutions [1].

In this contribution, we propose a facile batch-scale production of nanostructured cobalt ferrite (CoFe<sub>2</sub>O<sub>4</sub> - CFO) to sustain the large-scale production of novel rare-earth free permanent magnets. The proposed production is based on the design of tailored milling process of CFO powders produced by solid state reaction [2]. Two different calcination temperatures (1120 K and 1320 K) followed by milling in two steps, reducing the milling media size, were chosen. CFO nanoparticles with crystallite size of 33 nm, after the first milling step and mean particle size of 9 nm after the second milling step was achieved. The results from the magnetic characterization, performed by evaluating both the dynamic and static properties, show how the milling process affect the microstructure, and what the strengths and issues of the process are. The obtained energy product, (BH)<sub>max</sub>, which is the figure of merit for permanent magnets was found for randomly oriented powders over 2 MGOe. In principle, this value can be significantly further increased by orienting the nanograins under the application of an external magnetic field. This result makes this material extremely appealing as a building block to design novel permanent magnets alternative to RE-based ones, at least in the intermediate region of the energy product map, where the latter are currently employed simply because standard ferrites do not have large enough energy product.

[1] A. Lopez-Ortega; E. Lottini; C. de Julian Fernandez, C. Sangregorio, Chem. Mater. 27, 4048-56 (2015).

[2] P. Galizia, M. Cernea, V. Mihalache, L. Diamandescu, G. Maizza, C.130, 327-335 (2017).

ID-277

**Structure and magnetic properties of Fe<sub>67</sub>Co<sub>20</sub>B<sub>13</sub> alloy after crystallisation of amorphous ribbon by isothermal annealing with ultra-rapid heating**

*M. Kowalczyk<sup>1</sup>, J. Ferenc<sup>1</sup>, P. Zackiewicz<sup>2</sup>, A. K. Burian<sup>3</sup>, J. Kuśmierczyk<sup>1</sup>, T. Kulik<sup>1</sup>*

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<sup>3</sup> Department of Functional Materials, Institute of Non-Ferrous Metals

The Fe<sub>67</sub>Co<sub>20</sub>B<sub>13</sub> (at. %) metallic glass in the form of ribbon was subjected to isothermal annealing between two hot stainless steel blocks. This technique allowed to heat up the ribbon to the final temperature within a fraction of a second. The annealing temperature was from 340°C to 515°C, and annealing time was between 1 second and 60 minutes. The structure was investigated with X-ray diffractometry and DSC calorimetry. Hysteresis loops were recorded by quasi-static hysteresis loop recording and vibrating sample magnetometry. On the basis of this experiment, structure and soft magnetic properties were correlated, and optimum heat treatment regimes were determined. The results of ultra-rapid heating were compared to structure and properties of conventionally annealed samples of the same alloy, and the properties of the rapidly heated alloy were more attractive. Although the alloy after ultra-rapid heat treatment was significantly crystallised, in the optimally treated state it exhibited coercive field of only about 20 A/m. The saturation induction was of 1.88 T, which makes this alloy attractive for applications where soft magnetism and high induction are desired.

ID-389

**The magnetocaloric effect of bulk samples of Co-doped Ni-Mn-Sn Heusler alloys***M. Drobosyuk**Chelyabinsk State University*

The aim of this work was to investigate the magnetocaloric effect in Co-doped Ni-Mn-Sn Heusler alloys near the room temperature.

Polycrystalline ingots with nominal compositions  $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{39}\text{Sn}_{11}$  ( $x = 5; 6; 7; 8$ ) were prepared by arc-melting method in argon atmosphere. Weight loss is no more 0.5%. Samples ( $6 \times 3 \times 0.75$  mm) were cut from the middle part of ingots. The composition of the samples was determined by EDXRF spectrometer ARL QUANT'X.

The Curie temperature was determined from the low-field (50 Oe) magnetization curves measured by self-made magnetometer.

The magnetocaloric measurements were performed by the setup produced by AMT&C. In this setup, the adiabatic temperature change  $\Delta T_{\text{ad}}$  of the sample was registered by the direct method by means of the thermocouple. The magnetic field up to 20 kOe was produced by Halbach permanent magnet and was measured by the Hall probe. Signals from the thermocouple and the Hall probe were recorded simultaneously that allowed to measure  $\Delta T_{\text{ad}}$  as a function of magnetic field  $H$ . The value of the magnetocaloric effect of Samples 2, 3, 4 at the temperature range between 300 and 360 K are no more than 0.4 K. The maximum value of the magnetocaloric effect of the Sample 1 is 0.69 K observed near the Curie temperature  $T_C$ . The four samples of Heusler alloys with nominal composition  $\text{Ni}_{50-x}\text{Co}_x\text{Mn}_{39}\text{Sn}_{11}$  ( $x = 5; 6; 7; 8$ ) were studied. All samples are in martensite phase at room temperature. With the increasing of Co atoms the Curie temperature shown small increasing and its value are 387, 440, 442, 450 K for Samples 1, 2, 3, 4 respectively. The maximum value of the magnetocaloric effect is no more the 0.7 K for external magnetic field up to 2 T. Moreover, these alloys are not suitable for room temperature technology. We guess that the samples should be annealing at temperature more than 1100-1200 K for 3-5 days to be suitable for the magnetic refrigeration at the room temperature.

ID-437

**Structure and magnetic properties of alloys  $(\text{Nd}_{1-x}\text{Ce}_x)(\text{Fe}_{1-y}\text{Co}_y)_{11}\text{Ti}$  ( $0 \leq x \leq 0.3$ ,  $y = 0; 0.25$ ) produced by melt spinning***M. Zheleznyi, I. Shchetinin, A. Savchenko, A. Bazlov, E. Zanaeva**National University of Science and Technology "MISIS"*

According to the first principles calculations [1], magnetically hard materials based on the intermetallic compounds  $\text{R}(\text{Fe},\text{M})_{12}$  (where  $\text{R} = \text{Nd}$  or  $\text{Ce}$ ,  $\text{M} = \text{Ti}$  or  $\text{Co}$ ) with the structural  $\text{ThMn}_{12}$ -type have high values of spontaneous saturation magnetization, Curie temperature, constant and field of uniaxial magneto-crystalline anisotropy. Presumably, partial replacement of neodymium ions by cerium ions in the compound  $\text{NdFe}_{11}\text{Ti}$  promotes an increase in the basic magnetic hysteresis properties. It was shown in article that quenching from the liquid state of the  $\text{NdFe}_{11}\text{Ti}$  alloy leads to a single-phase state with a dispersed structure (the average grain size was about 120 nm). In this connection, the study of structural transformations and magnetic properties of alloys  $(\text{Nd}_{1-x}\text{Ce}_x)(\text{Fe}_{1-y}\text{Co}_y)_{11}\text{Ti}$  (where  $0 \leq x \leq 0.3$ ,  $y = 0; 0.25$ ), quenched from the liquid state, is an actual problem.

The investigated alloys were obtained by arc melting in an argon atmosphere followed by quenching from the liquid state, which was carried out on a DVX-II melt spinning machine. The elemental composition of the samples was determined on an X-ray fluorescence spectrometer with wave dispersion Rigaku ZSX Primus II, X-ray diffraction studies were carried out on a Rigaku Ultima IV diffractometer ( $\text{CoK}\alpha$  radiation) using the Rigaku PDXL 2 software. The microstructure of the cast alloys was investigated using a scanning electron microscope TescanVega 3SB, equipped with an attachment for energy-dispersive elemental microanalysis. The magnetic hysteresis properties of the samples were determined using a VSM-250 vibrational magnetometer in an external magnetic field of 20 kOe. As a result of the research, it was found that after quenching from the liquid state to the copper drum rotated at a linear velocity of 30 m / s, the alloys contained up to 90% of the main magnetically solid phase with the  $\text{ThMn}_{12}$  crystal lattice (Space group:  $I4/mmm$ ), the average grain size being 100-150 nm. An increase in the content of cerium in quenched  $(\text{Nd}_{1-x}\text{Ce}_x)(\text{Fe}_{1-y}\text{Co}_y)_{11}\text{Ti}$  alloys leads to an increase in the values of the main magnetic hysteresis properties.

The work was supported by the Ministry of Education and Science of the Russian Federation in the framework of the grant of the President of the Russian Federation to support young Russian scientists (Grant No. MK-3616.2017.2).

[1] Körner, Krugel, Elsässer // Sci. Rep. 6, 24686 (2016).

ID-451

**Novel relaxor ferroelectric-like behavior in BaTiO<sub>3</sub> and PbTiO<sub>3</sub> doped glasses for energy storage applications***M. El-Desoky<sup>1</sup>, A. Harby<sup>1</sup>, A. E. Hannora<sup>2</sup>, M. S. Al-Assiri<sup>3,4</sup>,*<sup>1</sup> Faculty of science, Suez university, Egypt<sup>2</sup> Department of Science and Mathematical Engineering, Faculty of Petroleum and Mining Engineering Suez University, Suez, Egypt, 43721<sup>3</sup> Physics Department, College of Science and Arts, Najran University, Najran, KSA<sup>4</sup> Promising Center for Sensors and Electronic Devices (PCSED) Najran University, KSA.

In this paper, glass samples of composition  $10_x\text{BaTiO}_3-x\text{PbTiO}_3-60\text{V}_2\text{O}_5-30\text{B}_2\text{O}_3$  with  $x=2.5, 5$  and  $7.5$  mol% were prepared by conventional melt quenching technique. The glasses were characterized by using X-ray diffraction (XRD), differential scanning calorimetry (DSC), High resolution transmission electron microscope (HRTEM), Raman scattering, dielectric spectroscopy as well as measuring ferroelectric hysteresis loops. XRD and DSC were used to emphasize the glassy nature of the present sample. Diffraction spots from clusters are clearly observed using HRTEM, which is presumably from polar clusters (PCs). The Raman spectra show a peak (Boson peak) at low frequency which is associated with the existence of intermediate range order such as PCs. The glass samples show relaxor ferroelectric-like behavior which is a novel phenomenon in the field of glass science. The existence of distorted BaTiO<sub>3</sub> and PbTiO<sub>3</sub> PCs embedded in the glass matrix is responsible for the appearance of this behavior. P-E hysteresis loop for the present glasses at room temperature exhibits ferroelectric-like shape loop with large values of remnant polarization ( $P_r$ ) and coercive field ( $E_c$ ). Also, the present glass samples show high energy storage density, which makes it good candidates for energy storage applications.

ID-461

**Structural and magnetic properties of Fe-X (X = Co, Cu) nanoclusters by density functional theory calculations***C. Cutrano, C. Lekka**University of Ioannina*

We present results from density functional theory calculations referring to the magnetic properties of 13, 55, 147 and 309 atoms Fe-X (with magnetic Co and non-magnetic Cu substitutions) icosahedral nanoclusters. Aiming in finding the nanocluster with the optimum magnetic moment (MM) we explored the various sizes considering several compositions and atomic conformations for Fe with Co and Cu substitutions. Starting with the FeCu nanoclusters, it comes out that configurations with agglomerated Fe atoms inside the Cu-Fe and the pure Cu surface shell are energetically favoured while the highest magnetic moment, 3.2 mB on the Fe atom, was found in the Cu<sub>12</sub>Fe case with the Fe atom located at the surface cell. In addition, as the size of the cluster increases the MM converges to the corresponding Fe monolayer value on Cu(111). The magnetic moment is mainly due to Fe's spin up - down electronic density of states difference close to the Fermi level (EF). In particular, the spin-up Fe d electronic density of states are fully occupied yielding wavefunctions with homogeneous charge distribution and Fe 4p occupation while the spin-down is almost unoccupied exhibiting dangling bonding states close to EF. The structural and magnetic properties of the Fe nanoclusters with magnetic Co substitutions were also evaluated. Contrary to Cu<sub>12</sub>Fe, Co<sub>12</sub>Fe is more stable when Fe is in the shell and the spin are coupled ferromagnetic. The electronic properties reveal that the Fe 3d states are strongly hybridize with the Co 3d for both spin up and spin down states. In agreement to CuFe case, Co<sub>12</sub>Fe shows the greatest MM that converges towards the fcc FeCo (111) thin films as the size of the cluster increases. These results could be used for the design of environmental sustainable smart alloys with superior magnetic properties e.g. by depositing Fe or FeCu on Cu nanoclusters or including new elements that provide the possibility of keeping the Fe Spin up-down electronic occupation difference close to EF.



ID-466

**Structural and multiferroic properties of nanostructured strontium doped bismuth ferrite***R. F. Gharib, M. M. El-Desoky, M. S. Ayoub**Physics Department, Faculty of Science, Suez University, Suez, Egypt*

Multiferroic of  $\text{Bi}_{1-x}\text{Sr}_x\text{FeO}_3$  ( $\text{BiSrFeO}_3$ ) ( $x = 0.10, 0.15, 0.20$  and  $0.25$  mol%) nanoparticles were prepared using solid-state reaction method. The nanostructural, Mössbauer spectroscopy and multi-ferroic properties of the prepared samples were investigated. X-ray diffraction (XRD) patterns show the formation of  $\text{BiSrFeO}_3$  with single-phase rhombohedral-hexagonal structure. The obtained results showed that all  $\text{BiSrFeO}_3$  nanoparticles are ferroelectric in character. Ferroelectric properties of  $\text{BiFeO}_3$  were found to change with  $\text{Sr}^{2+}$  ions substitution. Improvement of the magnetization of  $\text{BiFeO}_3$  is achieved by  $\text{Sr}^{2+}$  ions for  $x = 0.25$  mol%. At room temperature, remnant magnetization enhanced more than its initial value. The simultaneous occurrence of ferroelectric and ferromagnetism hysteresis loops in  $\text{BiSrFeO}_3$  multiferroic nanoparticles system at room temperature makes it a potential candidate for information storage and spintronics.

ID-489

**A new strategy for designing exchange coupled nano-heterostructures with high energy product**

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Permanent magnets are key elements for many technological devices that are largely used in everyday life, such as electronic devices, hard disks, automotive, wind turbines, and hybrid electric vehicles. The most powerful magnets currently used in a wide part of industrial necessities, comprise Rare Earth (RE) elements, which are expensive, harmful to the environment and present a high supply risk. [1] At present, a strong research activity is thus focused on finding viable alternatives to RE-based permanent magnets, which can allow their replacement at least in all those applications where high performances are not strictly required. This performance is determined by the magnetic energy density that can be stored within the material, which is represented by the maximum energy product  $(BH)_{max}$ . A significant enhancement of the magnetic performance of traditional ferrite nanoparticles (single phase), can be obtained by reducing the grain size to the nanoscale. Moreover, a further improvement can be achieved producing heteronuclear nanoparticles (NPs), whose magnetic properties are driven by inter or intraparticle exchange – effects, like exchange bias or spring magnet. [2] In this work we present and discuss, for the first time, the formation of  $Fe_xCo_{1-x}/CoFe_2O_4$  nanoparticles by a thermal decomposition method which uses metal oleates as precursors (Iron - cobalt and sodium oleate). The characterization of the obtained nanopowders by Transmission electron microscopy (TEM), Powder X-Ray diffraction (XRD), Dispersive Spectroscopy (EDS), Electron Energy Loss Spectroscopy (EELS) and X-Ray Photoelectron Spectroscopy (XPS), shows that polyhedral nanoparticles with coexistence of soft  $Fe_xCo_{1-x}$  alloy and non-stoichiometric hard  $Co_xFe_{3-x}O_4$  were obtained. Thermogravimetric (TGA) analysis demonstrated that controlling the thermal stability of the reactants in the presence of an excess of Sodium Oleate (NaOL), nanoparticles with different morphology, architecture (core-shell or heterodimers), crystal structure and composition could be obtained. Furthermore, increasing  $Co^{2+}$  concentration in the cobalt ferrite, we succeeded in modulating the heteronuclear nanoparticles's magnetic properties reaching, at room temperature,  $(BH)_{max}$  value of 15.7 kJ/m<sup>3</sup>.

[1] J. Sort, et al. Appl. Phys Lett. 79, 1142 (2001).

ID-504

**Perpendicular magnetized GMR spin valves with a synthetic antiferromagnetic reference layer on flexible substrates**M. Hassan,<sup>1,2\*</sup> G. Barucca<sup>2</sup>, S. Laureti<sup>1</sup>, O. Lik<sup>3</sup>, N. Safonova<sup>3</sup>, M. Albrecht<sup>3</sup>, G. Varvaro<sup>1</sup><sup>1</sup>Istituto di Struttura della Materia, CNR, NM<sup>2</sup>-Lab, Monterotondo Scalo (Roma), 00015, Italy<sup>2</sup>Università Politecnica delle Marche, Dipartimento SIMAU, Via Brecce Bianche, Ancona 60131, Italy<sup>3</sup>Institute of Physics, University of Augsburg, Universitätsstraße 1 Nord, D-86159 Augsburg, Germany

Flexible electronics has received a great deal of attention over the past decades owing to its outstanding potential in many technological fields including energy, optics, sensors and information storage, among others [1,2]. Flexible devices provide wide advantages over their conventional rigid-substrate counterparts, such as the ability to bend and adjust the shape of a device, a lower weight and lower costs. To expand the domain of flexible electronics, a significant effort has been recently pursued to develop spin-related electronic devices on flexible substrates [2]. In this work, we investigated the possibility to obtain high-quality GMR heterostructures with perpendicular magnetic anisotropy on flexible substrates by exploiting a transfer-and-bond approach where the heterostructure is first deposited on a rigid substrate covered with a weakly-adhering layer, and then transferred on an adhesive and flexible substrate by a simple mechanical peel-off step, similar in nature to the methods used for the exfoliation of graphene and other materials. For this purpose, a 10-nm Au layer was first deposited by DC-sputtering onto a thermally oxidized Si/SiO<sub>x</sub> substrate due to the low adhesion coefficient of Au on such a substrate. On top of the Au layer, [Co/Pd]<sub>4</sub>/Ru/[Co/Pd]<sub>4</sub>/Cu(x nm)/[Co/Pd]<sub>2</sub> GMR stacks (x = 2 and 5 nm) with a fully compensated [Co/Pd]<sub>4</sub>/Ru/[Co/Pd]<sub>4</sub> synthetic antiferromagnetic reference layer were deposited at room temperature and the magnetic and magneto-transport properties were investigated as a function of the Cu spacer thickness. The same GMR stacks were also directly deposited on Si/SiO<sub>2</sub> substrates as comparison. All the samples present a clear perpendicular anisotropy even when deposited on the Au layer. The Au-free reference samples show the expected field-dependent magnetization response, the GMR ratio assuming a maximum value of about 5% for a Cu thickness of 2 nm. When the stack is deposited on Au, we observed a worsening of the magnetic properties when a thin Cu layer is used, likely because of the presence of exchange interactions between the reference and free layers induced by the rougher Au interface. However, for thicker Cu spacers, the magnetic properties are maintained and a GMR ratio of about 2% is achieved. Such a stack was successfully transferred on an adhesive tape, thus confirming that such a transfer-and-bond approach can be pursued to obtain complex spintronic heterostructures on flexible substrates.

[1] Flexible Electronics: Materials and Applications, W.S. Wong and A. Salleo, Eds., Springer (2009)

[2] D. Makarov et al. Appl. Phys. Rev. 3 (2016) 011101

**Wednesday 4 July afternoon - 17:30/18:30**

Poster Session 3  
**APPLICATIONS**  
Chair: V. Kamalakar Mutta

ID- 60

## Composite materials for catalytic methane reforming

G. Xanthopoulou<sup>1</sup>, S. Tungatarova<sup>2</sup>, K. Karanasios<sup>1</sup>, T. Baizhumanova<sup>2</sup>, Z. Zheksenbaeva<sup>2</sup>, M. Zhumabek<sup>2</sup>, G. Kaumenova<sup>2</sup>

<sup>1</sup> Institute of Nanoscience and Nanotechnology, NCSR Demokritos

<sup>2</sup> D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry; al-Farabi Kazakh National University

Self-propagating high-temperature synthesis (SHS) method is used worldwide for the low-cost production of advanced ceramics, intermetallics, catalysts and magnetic materials. The method exploits self-sustaining solid-flame combustion reactions for the internal development of very high temperatures over very short periods. It therefore offers many advantages over traditional methods such as much lower energy costs, ease of manufacture and capability for producing materials with unique properties and characteristics.

The basic principles of SHS can be summarized as follows: rapid auto wave combustion-like self-sustaining reactions yielding resultant products of desired composition and structure, complete or partial elimination of external energy supply by the utilization of the internal heat released in the chemical reactions, control of the process rate, temperature, degree of conversion, composition and structure of products by variation in the rates of heat release and transfer. Very high interest to SHS catalyst can be explained by high activity of catalysts prepared by this methods and advantages of SHS method in comparison with traditional methods of preparation of catalysts.

Processing of natural gas into motor fuel has become one of the major problems of chemistry. Partial oxidation and dry reforming of CH<sub>4</sub> attract a great attention in recent years. Resistant to temperature extremes and thermal shocks is one of the most important requirements for catalysts. Works on research of intermetallic compounds as a contact mass for conversion of methane were carried out. Mixtures of the (Ni(NO<sub>3</sub>)<sub>2</sub> - Co(NO<sub>3</sub>)<sub>2</sub> - Al(NO<sub>3</sub>)<sub>3</sub> - Mg(NO<sub>3</sub>)<sub>2</sub>) salts are used for the synthesis of catalysts. The reactions resulting in the formation of NiCo<sub>2</sub>O<sub>4</sub>, Co<sub>2</sub>AlO<sub>4</sub> and CoAl<sub>2</sub>O<sub>4</sub> spinels and AlCo, AlNi<sub>3</sub> intermetallic compounds occur at preparation of samples by solution combustion synthesis. Investigation of the activity of catalysts based on the initial mixture of metal oxides produced in the solution combustion synthesis process was carried out in the reaction of carbon dioxide conversion and partial oxidation of methane. 100% methane conversion at 750°C was carried out on the catalyst, whereas the conversion of CO<sub>2</sub> reached 81.7% at 900°C. H<sub>2</sub> yield reached 99.2%, yield of CO - 99.1% in the ratio of H<sub>2</sub>/CO = 1.2. Thus, effective catalysts for the production of synthesis gas from methane have been developed.

ID-130

**First-principles study of new series of quaternary Heusler alloys CsSrCZ (Z=Si,Ge,Sn,PAs,and Sb)***A. Bouabca<sup>1</sup>, H. Rozale<sup>1</sup>, X. Wang<sup>2</sup>, A. Sayede<sup>3</sup>, A. Amar<sup>1</sup>*<sup>1</sup> *Condensed Matter and sustainable development Laboratory (LMCDD)*<sup>2</sup> *School of Physics and Electronic Engineering*<sup>3</sup> *UCCS, CNRS-UMR 8181, Université d'Artois, Faculté des Sciences*

The structural, electronic, magnetic, and thermal properties of new quaternary Heusler alloys CsS-rCZ ( $Z^{1/4}$ Si, Ge, Sn, P, As, and Sb) were investigated using the full-potential linearized augmented plane wave (FPLAPW) within the generalized gradient approximation (GGA) and GGA plus modified Becke and Johnson as the exchange correlation. The results showed that all Heusler compounds were stable in Type (I) structure. The CsSrCZ ( $Z^{1/4}$ Si, Ge, Sn) compounds had a nearly HM characteristic, and CsSrCZ ( $Z^{1/4}$ P, As, Sb) compounds were true half-metallic (HM) ferromagnets. The strong spin polarization of p orbital for C, Si, Ge, Sn, P, As, and Sb atoms is found to be the origin of ferro-magnetic. The half-metallicity is preserved up to a lattice contraction of 3.45%, 1.69%, 1.69%, 7.16%, 7.16%, and 11.2% for all six quaternary Heusler compounds. We also investigated the thermal effects using the quasi-harmonic Debye model.

ID-221

**Application of mechanically alloyed Mn-Al metallic particles to wastewater treatment: a comparative investigation of chemical and bacterial approaches to dye degradation in residual textile waters***M. Abolighasemabadi<sup>1</sup>, E. Pineda<sup>1</sup>, L. Escoda<sup>2</sup>, J. J. Suñol<sup>2</sup>, K. Doelle<sup>3</sup>, S.-G. Chatterje<sup>3</sup>*<sup>1</sup> *Departament de Física, Universitat Politècnica de Catalunya*<sup>2</sup> *Departament de Física, Universitat de Girona*<sup>3</sup> *Department of Paper and Bioprocess Engineering, State University of New York College of Environmental Science and Forestry*\*Corresponding Author(s): [eloi.pineda@upc.edu](mailto:eloi.pineda@upc.edu)

Residual dye compounds in textile wastewater are one of the most critical sources of environmental pollution because of their visibility and potential carcinogenic properties. The use of Mn-Al nano-crystalline particles has been shown to provide a rapid and convenient degradation of these dye compounds [1]. It is also expected to be a low-cost method for the degradation of many types of contaminating compounds and not just residual textile dyes. This work analyzes the efficiency of Mn-Al metallic powders for degrading azo dyes and compares the results with the ones obtained in a pilot scale trickling filter. Several batches of Mn-Al metallic powders were produced using a ball-milling process, applying different durations of the milling operation. This resulted in a set of batched powders that differed from each other in terms of their internal particle structure as characterized by X-ray diffraction and electron microscopy. The ability of these powders to act as decolorization materials was assessed by degradation experiments of Orange G and Orange II azo dyes in aqueous solutions, obtaining fast kinetics with reaction times among the shortest when compared to the results reported using other decolorizing materials. The effect of various parameters such as initial pH, dye concentration, and temperature were studied. The electrochemical and corrosion properties of the Mn-Al metallic powder seemed to be the key factors explaining the high decolorization efficiency of these materials.

The ability of biological agents to treat textile wastewater streams was also examined. The bacterial microorganisms selected in the trickling filter presented the ability to remove dye under aerobic conditions at pH values between 6 and 7.5 but with low efficiency. The bacteria microorganisms were able to remove mono-azo dyes but no other chemically different dyes. Both bacterial and metallic powder approaches appear to be viable options for the treatment of textile wastewaters, though lower rates of dye removal were observed with the bacterial approach as compared to the Mn-Al powder method. A discussion on possible combinations of these two processes to increase efficiency on a wide range of temperature and pH conditions will be also discussed in this work.

[1] M. AboliGhasemabadi et al. J. Alloys Compd. 741 240-245 (2018)

ID-228

**Influence of doped Mn-Al nanocrystalline powders produced by ball-milling in the degradation efficiency of azo dye***W. B. Mbarek<sup>1</sup>, E. Pineda<sup>2</sup>, L. Escoda<sup>3</sup>, J. J. Suñó<sup>3</sup>, M. Khitouni<sup>1</sup>*<sup>1</sup> *Université de Sfax*<sup>2</sup> *Departament de Física, Universitat Politècnica de Catalunya*<sup>3</sup> *Departament de Física, Universitat de Girona*\*Corresponding Author(s): [benmbarekwael@yahoo.com](mailto:benmbarekwael@yahoo.com)

Azo compounds are one of the most common families of dyes used in textile and leather treatments. An important step during the treatment of water polluted by these compounds, is the degradation of the compounds by decomposition of the N=N bonds, producing the de-colorization of the water.

In this work, we present the decolorization of reactive black 5 solutions using Mn-Al-Co and Mn-Al-Fe nanostructured powders produced by ball milling. The morphology and the phase structure of the metallic powders were characterized by scanning electron microscopy coupled with EDS microanalysis and by X-Ray diffraction. The decolorization efficiency of reactive black 5 solutions was assessed by monitoring the dye degradation by ultraviolet visible absorption spectrophotometry. Co doped Mn-Al showed a fast kinetics and high efficiency. 40 mgL<sup>-1</sup> of dye solution was successfully decolorized in 5 min using 0.25 g / 100 mL of powders, even in neutral pH conditions. However, Mn-Al-Fe powders with respecting same conditions were successfully decolorized in 10 min. The efficiency is higher than those found with Mn particles. The efficiency was also checked in other azo-dyes solutions. To summarize, nanocrystalline Co-doped Mn-Al exhibits superior properties, such as high reactivity and efficiency, wide applicability, good reusability and low corrosion loss, in comparison with Fe-doped in the same alloys.



ID-286

## Electrodeposition of cobalt-substituted calcium phosphate coatings on $Ti_{22}Nb_6Zr$ alloy for bone implant applications

R. Drevet<sup>1</sup>, Y. Zhukova<sup>1</sup>, S. Dubinskiy<sup>1</sup>, A. Kazakbiev<sup>1</sup>, V. Naumenko<sup>1</sup>, M. Abakumov<sup>1</sup>, J. Faure<sup>2</sup>, H. Benhayoune<sup>2</sup>, S. Prokoshkin<sup>1</sup>

<sup>1</sup> National University of Science and Technology "MISIS"

<sup>2</sup> URCA

This work investigates the electrodeposition of cobalt-substituted calcium phosphate coatings on  $Ti_{22}Nb_6Zr$  alloy developed for bone implant applications [1,2]. The experimental conditions of the process are optimized to establish the link between the amount of cobalt ions introduced in the electrolytic solution and the amount successfully incorporated inside the calcium phosphate layer. The scanning electron microscope observations show the specific morphology of the electrodeposited coating linked to the cobalt addition. The phase composition analysis by X-ray diffraction reveals that the calcium phosphate coating is made of an apatite phase of low crystallinity. The corrosion behavior of the coated and uncoated  $Ti_{22}Nb_6Zr$  alloys is studied from polarization curves carried out in Hank's solution at 37°C, a physiological solution that mimics the inorganic composition of the body fluids. The results show that the cobalt-substituted calcium phosphate coating protects the surface of the titanium alloy against the corrosion reactions induced by the aggressive physiological environment. The specific impact of the cobalt substitution is discussed and the corrosion results are compared to those obtained from unsubstituted calcium phosphate coatings synthesized in the same experimental conditions. At last, the biocompatibility of this new implant surface is assessed in vitro by determining the cells survival after 24 h, 48 h and 72 h in contact with the electrodeposited coating.

[1] V. Sheremetyev, V. Brailovski, S. Prokoshkin, K. Inaekyan, S. Dubinskiy, Materials Science & Engineering C 58, 935-944 (2016).

[2] S.R. Paital, N.B. Dahotre, Materials Science & Engineering R 66, 1-70 (2009).

ID-356

**Heteropoly complex composite materials for oxidative conversion of alkanes***S. Tungatarova, T. Baizhumanova, Z. Zheksenbaeva, K. Kassymkan, R. Sarsenova, G. Begimova**D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry*

1-2,3%  $H_4SiMo_{12}O_{40}$ /aluminosilicate catalysts of polyfunctional action for oxidation, oxidative dehydrogenation and dehydroaromatization of methane have been developed. Optimal conditions for synthesis of products and physico-chemical properties of the catalysts have been determined. By TPR method was detected that treatment of catalysts in mixture ( $O_2$ , water vapor) at  $650^\circ C$  after reaction at  $650-800^\circ C$  regenerated all forms of structural oxygen which are specific for initial supported heteropoly acid (HPA). The catalyst was exposed the reduction processing by  $H_2$  or  $CH_4$  before dehydroaromatization of  $CH_4$ . Such processing plays the major role for increase the activity of catalyst. The studies of samples by XRD and TEM methods have been carried out for understanding of difference as a result of reduction by  $H_2$  or  $CH_4$ . Reduction in  $H_2$  proceeds through a stage of destruction of HPA after  $360^\circ C$  to  $MoO_3$ .  $MoO_2$  phase forms at  $500-600^\circ C$ .  $MoO$  is formed at temperatures above  $800-900^\circ C$ . The heating at reduction of HPA by  $CH_4$  at  $300^\circ C$  result in appearance of dispersed phase of  $H_{1,68}MoO_3$  (33-604), semi-transparent particles with compactings ( $40-60\text{\AA}$ ) yielding the ring-type micro diffraction pattern relating to  $MoC$  (8-384), and also agglomeration of particles of the dropwise type ( $20-50\text{\AA}$ ) relating to  $MoC$  (6-546). At heating at  $500^\circ C$  besides  $-MoC$  the high-temperature phase of carbon C-Lonsdeillite (19-268) in the form of large round semi-transparent particles was fixed. There are long resilient carbon nanotubes with preferential diameter  $500-800\text{\AA}$  together with  $-Mo_2C$  (35-787) at the further increase of temperature. TEM method has allowed determining the formation of  $Mo_2C$  at lower temperatures than it was revealed by XRD owing to dispersity of particles. Thus, formation of molybdenum carbide instead of  $MoO$  was preferentially in a hydrocarbon medium. Formation of carbides on a surface of catalysts promotes realization of aromatization of alkanes.

**Thursday 5 July morning - 10:00/11:00**

Parallel Session 1  
NANOSTRUCTURED MATERIALS IX  
Chair: W. Botta

**ID-500 (Invited)****Magnetic Fe-based nanoarchitectures**

*F. Sayed, N. Yaacoub, Z. Nehme, R. Busselez, Y. Labaye, F. Calvayrac, J.M. Greneche*

*Institut des Molécules et Matériaux du Mans, UMR CNRS, France*

For the last 30 years, great attention has been devoted to the development of nanosciences and nanotechnologies. Indeed, it includes (i) the elaboration procedures of nanomaterials under different morphologies, (ii) the characterization of their structural, chemical and physical properties to establish size dependent structure-physical properties correlations, (iii) the size dependent scale computer modelling and (iv) their potential applications. Among the different families of nanomaterials, magnetic ones have been particularly investigated as new behaviors result from confinement effects: it is important to emphasize that their magnetic properties are strongly dependent on the size, morphology and spatial distribution of individual nanoparticle and on the architecture of 2D-3D assemblies of nanounits, each unit corresponding to a nanograin.

Consequently, the strategy consists first in the fine and deep characterization of these nanomaterials using complementary multi-scale techniques and then in the modelling to better understand magnetic phenomena such as surface and interface effects, exchange bias and the role of dipolar interactions.

The main goal of the presentation is to illustrate this purpose from selected examples based on 1D, 2D and 3D magnetic nanostructures which have been carefully investigated and to report some relevant results established from computer modelling.

## ID-159

**Deformation of nanocrystalline PdAu and concurrent in-situ X- ray diffraction**

*M.J. Deckarm*<sup>1</sup>, *A. Leibner*<sup>1</sup>, *V. Dyadkin*<sup>2</sup>, *M. Majkut*<sup>2</sup>, *R. Birringer*<sup>1</sup>

<sup>1</sup> Saarland University

<sup>2</sup> ESRF

Scaling the grain size down to the low end of the nano scale (approximately 10nm) entails a dramatic change in mechanical properties (e.g. increased yield strength, tension-compression asymmetry, high strain rate and temperature sensitivity, lowered ductility), which is essentially attributed to grain confinement effects on the one hand and the massively increased influence of the grain boundary (GB) phase on the other hand; after all, at these small grain sizes, GBs occupy more than 15% of the total volume.

In a recent study, Grewer et al. [1] examined the deformation of nanocrystalline PdAu in an in-situ experiment using a combination of optical strain and synchrotron-based X-ray diffraction measurements. The central result was a quantitative estimate of the contributions of elasticity, stress driven GB migration and dislocation glide to the overall deformation. However, the sum of these processes amounted to less than 35% of the overall plastic strain which led to the conclusion that the plastic deformation is dominated by processes in the core region of the GBs.

In continuation of this work, we explored the effects of different strain rates and stress states, respectively, by a series of in-situ X-ray diffraction experiments at beamline ID11 at the ESRF. To extract structural information from the scattering data, the whole powder pattern modelling approach from Scardi and Leoni [2] was adopted to the examined material, which provided high temporal resolution information on the evolving strain and stress state in the crystalline phase, as well as on texture formation, grain growth or stacking fault density changes. Simultaneously, the macroscopic stress- strain evolution was obtained from optical displacement and force measurement. By juxtaposing information on the samples macroscopic deformation behaviour and the evolution of the crystalline fraction, we study how the ensemble of nanocrystallites interacts with the embedding GB phase.

We could, e.g., show that the strain rate sensitivity of nanocrystalline PdAu is not reflected by the crystalline phase and therefore can be regarded as an effect originating from viscoplastically deforming GBs.

[1] M. Grewer et al., *Mechanics of Materials*, 114, 2017, 254-267

[2] Scardi, P & Leoni, M., *Acta crystallographica. Section A, Foundations of crystallography.*, 57., 2001, 604-613.

ID-439

## In-situ and real time observation of crystallisation-induced stress development during the early growth stages of $\text{Mo}_{1-x}\text{Si}_x$ alloys

A. Michel<sup>1</sup>, B. Krause<sup>2</sup>, G. Abadias<sup>1</sup>, A. Fillon<sup>3</sup>, J. Colin<sup>1</sup>, T. Baumbach<sup>1,4</sup>

<sup>1</sup> Institut Pprime, Département de Physique et Mécanique des Matériaux

<sup>2</sup> Institut für Photonenforschung und Synchrotronstrahlung (IPS), KIT

<sup>3</sup> INSA, UMR CNRS 6226, équipe chimie-métallurgie

<sup>4</sup> Laboratorium für Applikationen der Synchrotron- strahlung (LAS)

The deposition of metallic layers on silicon still is an attractive field of research, due to potential applications in nanoelectronics. Interfacial silicide formation is a subject of prime interest, in a context where device sizes are nowadays reduced to a few nm, and the silicide layer steers the development of film texture, microstructure and surface morphology. The kinetics of phase transitions during formation of such small-scale systems are essential, however, their experimental observation remains challenging. To this purpose, we developed a strategy of coupled in-situ diagnostic tools during sputtering growth.

Magnetron sputtering deposition, due to the high deposition energy, meets out-of-equilibrium conditions, while interfacial reactions between substrate and films are favoured. Experimentally, a 2D growth is observed when depositing low mobility metals onto neutral substrates (native oxide covered Si). For the Mo-on-Si system, an interfacial reaction promotes the 2D growth, while an amorphous interfacial layer is stabilized. At a critical thickness (~2 nm), an abrupt amorphous-to-crystalline phase transformation occurs, involving the backwards crystallisation of most of the deposited layer towards the equilibrium bcc phase [1].

We investigated the deposition of  $\text{Mo}_{1-x}\text{Si}_x$  alloys, using three in situ methods simultaneously combined [2] during magnetron sputtering deposition: substrate curvature measurement using a multiple-beam optical stress measurements (MOSS), X-ray reflectivity (XRR), and X-ray diffraction (XRD) measurements. This unique methodology allows to directly relate the stress evolution, obtained from MOSS, and the time-dependent film thickness and roughness development [3], with the crystal formation.

The measurements provide direct evidence of an amorphous-to-crystalline transition, at a critical thickness related to Si content  $x$ , and associated with a tensile stress build-up and surface roughening. This phase transformation is thermodynamically driven, the metastable amorphous layer being initially stabilized by the contributions of surface and interface energies. A quantitative analysis of the XRD data, supplemented by simulations of the transformation kinetics, unveils an interface-controlled crystallization process.

[1] Fillon, A.; et al., Phys. Rev. Lett. 2010, 104, 096101

[2] B. Krause et al., ACS Appl. Mater. Interfaces 8 (2016), 34888–34895

[3] M. Kaufholz, et al., J. Synchrotron Radiat. 2015, 22, 76–85

Thursday 5 July morning - 10:00/11:00

Parallel Session 2  
**METALLIC GLASSES XI**  
Chair: J. Eckert

## ID-132 (Invited)

**A structural study of a rejuvenation effect in amorphous Gd-Co metal by anomalous x-ray scattering**

*S. Hosokawa*<sup>1</sup>, *J.R. Stellhorn*<sup>1</sup>, *Y. Yamazaki*<sup>2</sup>, *H. Kato*<sup>3</sup>, *N. Blanc*<sup>4</sup>, *N. Boudet*<sup>4</sup>

<sup>1</sup> Kumamoto University

<sup>2</sup> National Institute of Technology, Ube College

<sup>3</sup> Tohoku University

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Recently, much attention has been achieved on the rejuvenation behaviors in metallic glasses. It was found that repeated thermal changes induce this effect. According to Ketov et al. [1], there would be distributions of thermal expansion coefficient if a glass is inhomogeneous. In such a glass, shear forces are induced between the parts with large and small volume changes by repeated temperature changes, and there a rejuvenation happens. Therefore, it is suggested that the larger an inhomogeneity is in a glass, the more prominent the rejuvenation is. The validity of the above logic is currently an important subject of discussion. In our group, a study of structural relaxations was performed on a Gd<sub>65</sub>Co<sub>35</sub> metallic glass, and a prominent peak was found in the  $\beta$  relaxation [2], indicating a large structural inhomogeneity in this metallic glass. Anomalous x-ray scattering (AXS) is an excellent method for investigating the short- and intermediate- range order (SRO and IRO). We developed a new detecting system suitable for AXS using the third- generation synchrotron radiation facilities, at BM02 of the ESRF [3].

The Gd<sub>65</sub>Co<sub>35</sub> metallic glass was manufactured at Tohoku University, Japan, by a splat quenching from a molten mixture under high-purity Ar atmosphere. A part of the sample was treated by a repeated temperature changes by forty times between the room- and liquid N<sub>2</sub> temperatures for causing a rejuvenation effect. In the differential structure factors,  $\Delta_k S(Q)$ , a prominent rejuvenation effect is observed around the Co atoms, while almost no effect is seen around the Gd atoms. The experimentally obtained  $\Delta_k S(Q)$ 's and  $S(Q)$ 's and the subsequent RMC simulation give us detailed information about the partial structural SRO and IRO of the as-quenched and thermally treated Gd<sub>65</sub>Co<sub>35</sub> metallic glasses. The well-analyzed partial structure factors  $S_{ij}(Q)$ , partial pair- correlation functions  $g_{ij}(r)$ , and the three-dimensional atomic configurations can clarify the role of the constituent elements for the rejuvenation effect. We discuss the relation between the structural inhomogeneity and thermal rejuvenation (thermal relaxation) of metallic glass with the viewpoint of the partial structures.

[1] S. V. Ketov et al., Nature 524, 200 (2015).

[2] Y. Yamazaki, PhD Thesis (Tohoku Univ., 2016).

[3] S. Hosokawa et al., Eur. Phys. J. Special Topics 208, 291 (2012); Z. Phys. Chem. 230, 313 (2016).



ID-127

**Rejuvenation in metallic glasses: high resolution electron microscopy study***L. Ivanov<sup>1</sup>, S. Ketov<sup>2</sup>, D. Luzguine-Luzgin<sup>3</sup>, J. Eckert<sup>2</sup>, A.L. Greer<sup>1</sup>*<sup>1</sup> *Department of Materials Science & Metallurgy, University of Cambridge*<sup>2</sup> *Erich Schmid Institute of Materials Science, Austrian Academy of Sciences*<sup>3</sup> *Advanced Institute for Materials Research, Tohoku University*

Bulk metallic glasses (BMGs) are materials of interest for both functional and structural applications [1]. However, the lack of macroscopic ductility limits their application fields. It was established that metallic glasses with structures closer to the liquid exhibit higher plastic strain than relaxed ones. Recently, a new method for metallic-glass rejuvenation was found [2]. The heterogeneous structure of metallic glasses on a nm scale, when subjected to temperature change, results in heterogeneous thermal expansion or contraction, inducing local stresses high enough for anelastic strains to occur. Cryothermal cycling appears to be an attractive and simple method to rejuvenate metallic glasses. The method appears also to be useful for wide variety of materials. However, the applicability boundaries of the method for metallic glasses are still unknown. Here we report a HRTEM study of the chemical and structural changes in  $Zr_{60}Cu_{20}Fe_{10}Al_{10}$ ,  $Zr_{60}Cu_{20}Co_{10}Al_{10}$ , and  $Zr_{60}Cu_{20}Ni_{10}Al_{10}$  (at.%) BMGs as a result of cryothermal cycling.

TEM studies were carried out with a Titan G2 60–300, equipped with X-FEG and Cs image corrector. The structural characterization of the amorphous materials was performed by evaluation of the atomic radial distribution function (RDF) which was directly computed from FFT patterns of the HRTEM images and compared with the ones obtained from SAED.

It was established that cryothermal cycling is a universal method for triggering structural changes in these glasses composed of mixtures of metallic elements only. BMGs of chosen compositions behave differently under cryothermal cycling, showing that it can work as a method for relaxation as well as rejuvenation of metallic glasses, and leading to improvement or degradation of mechanical properties. The nature of the bonding in metallic glasses appears to have a significant influence on the treatment outcome, for example the maximal plastic strain that can be achieved. Analysis of HRTEM images revealed heterogeneities in the composition and structure of the Fe-containing BMG after cryothermal cycling, with RDF peaks shifted indicating that the average atomic bond distances increased. This indicates the increase of general volume associated with rejuvenation in this glass. In contrast, such effects are not found in the apparently similar Ni-containing BMG.

[1] Y. Sun, A. Concustell, A.L. Greer, *Nature Reviews Materials* 1, 16039 (2016)

[2] S.V. Ketov, et al., *Nature*, 524, 200 (2015)

## ID-161

**The correlation between rejuvenation behavior and boson heat capacity peak of bulk metallic glass**

*H. Zhou, N. Nollmann, R. Hubek, M. Peterlechner, G. Wilde*

*Institute of Materials Physics, University of Münster*

Rejuvenation behavior and boson peak of  $\text{Pd}_{40}\text{Ni}_{40}\text{P}_{20}$  metallic glass influenced by severe plastic deformation are investigated for as cast and annealed states. It is shown that the structural enthalpy and fictive temperature could be both effectively recovered by high-pressure torsion, consistent with the strongly enhanced boson peak. Subsequently, the structural enthalpy and fictive temperature are used to analyze the correlations with boson peak height respectively, and the results show that the boson peak height is not only connected with the deformation-inducing excess volume accompanied with the shear-transformation zone but also related to the annealing-effecting excess volume located in the matrix. Finally, a universal linear function can be built between fictive temperature and boson peak height even under the combined influence of deformation and annealing. This link is quite significant because it provides a profound understanding of high-temperature relaxation and low-temperature boson peak, and further helps to predict each other if one is given.

Thursday 5 July morning - 10:00/11:00

Parallel Session 3  
**PHASE TRANSFORMATION I**  
Chair: M. Baricco

**ID-410 (Invited)****Stable and metastable crystalline phases in the Al-Ge and Al-Ce-Mn systems: structural characterization and formation mechanisms**

*M. Kaufman<sup>1</sup>, C.S. Kiminami<sup>2</sup>, W.J. Botta<sup>2</sup>, C. Bolfarin<sup>2</sup>, C. Francisco<sup>1</sup>, J. Jankowski<sup>1</sup>*

<sup>1</sup> Colorado School of Mines

<sup>2</sup> UFSCar - Federal University of São Carlos

The formation of microstructures containing desirable distributions of stable and/or metastable phases in a controlled and reproducible manner has remained a significant challenge to the rapid solidification community in its search for materials with superior mechanical properties. In this work, bulk Al-Ge and Al-Mn-Ce alloys have been produced using intermediate and rapid solidification methods and the resulting structures have been examined in detail using SEM, HRTEM and both x-ray and electron diffraction. For the Al-Ge alloys, the HRTEM results were combined with x-ray charge flipping to determine the details of the crystal structure of the metastable monoclinic phase, which is the easiest of four different metastable phases to form in this system. In addition, the rapid solidification of Al-Ge thin films that underwent laser-induced, localized melting has been examined using multi-frame dynamic transmission electron microscopy (DTEM), a nanosecond-scale TEM technique. By employing these complementary techniques, it is possible to gain a clearer understanding of the factors that control stable and metastable phase formation under near and far-from-equilibrium processing conditions.

## ID-122

**Mechanical spectroscopy as a tool to study first and second order transitions in metastable Fe-Ga alloys**

V. Palacheva<sup>1</sup>, G. Vuilleme<sup>2</sup>, D. Mari<sup>2</sup>, L.S. Golovin<sup>1</sup>

<sup>1</sup>NUST MISiS

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Temperature dependent measurements of internal friction and modulus of elasticity (E at bending and G at torsion), known as mechanical spectroscopy, are used in this work to detect phase transition in metastable Fe-Ga alloys during heating and cooling from room temperature to 850°C. Mechanical spectroscopy results obtained on torsional pendulum and dynamic mechanical analyzer are discussed together with the results of DSC, VSM and in situ neutron diffraction tests performed on the same materials. Three transient anelastic effects are recorded in the Fe-(26-28)at.%Ga alloys. These peaks correspond to the first order D03 → L12 → D019 → B2 phase transitions. The diffusion controlled disordering-ordering processes are also confirmed in the A2/D03, A1/L12, A3/D019 phases prior to the first order transitions between them. The presence of the dips, i.e., modulus minima at the transition temperatures suggests that a softening of the elastic constants in some directions triggers the transition. The L12 → D019 phase transition between two closed packed structures is accompanied by the internal friction peak due to a long-range motion of the Shockley dislocation. The second order transition - ordering of the A2 phase in Fe-(17-19)at.%Ga - is also accompanied by - shaped IF peaks and along with VSM and neutron diffraction data helps to characterize short range ordering, sometimes called as nano heterogeneities, in the Fe-Ga alloys.

## ID-140

**Kinetics of polymorphic transformations of pharmaceuticals induced by mechanical milling**

*J-F Willart<sup>1</sup>, P. Bordet<sup>2</sup>, M. Descamps<sup>1</sup>, E. Dudognon<sup>1</sup>, P. Martinetto<sup>2</sup>, W. Pagnoux<sup>1,2</sup>*

<sup>1</sup> UMET (Unité Matériaux et Transformations) UMR CNRS 8207

<sup>2</sup> Univ. Grenoble Alpes, CNRS

Mechanical milling of powders is a usual process used in the course of drug formulation to reduce the particle size. However this process may also change the physical state of the end product, leading sometimes to an amorphization and sometimes to a polymorphic transformation [1]. Amorphizations mainly occur when milling is performed below the glass transition temperature ( $T_g$ ) of the material while polymorphic transformations mainly occur when milling is performed above  $T_g$ .

It appears from the literature that amorphization kinetics generally obey an exponential relaxation law [2]. On the other hand, kinetics of polymorphic transformations have generally a sigmoidal shape characterized by long incubation time preceding a fast transformation stage. The origin of this striking difference remains an open question. Moreover, the physical mechanisms which are responsible for the quite long incubation preceding the polymorphic transformations are not yet understood.

We present here an investigation of a few pharmaceutical compounds (mannitol, sorbitol...) which give some new insights on the physical mechanisms which govern polymorphic transformations induced by mechanical milling. Mannitol is shown to undergo a polymorphic transformation  $b \rightarrow a$  upon milling whose kinetics is clearly sigmoidal [3]. This kinetic was followed in detail during the milling process itself through original real-time in-situ synchrotron X-ray diffraction experiments (ESRF / ID15.B). This makes it possible to detect striking tiny features of the transformation. In particular, a small fraction (2.5%) of the final form is found to develop rapidly and to remain stationary during the whole incubation time. This unexpected behaviour strongly suggests that the transformation results from a competition between  $b \rightarrow a$  and  $a \rightarrow b$  transformations of crystallites which depend on the physical state of neighbouring crystallites. This scenario was confirmed on sorbitol by showing that the incubation time of the transformation strongly shortens when the initial powder is seeded with a small fraction of the final polymorphic form  $a$ . It was also confirmed by numerical simulations of the above mechanism performed at the level of crystallites.

[1] J.F. Willart et al., *Molecular Pharmaceutics*, 5, 905 (2008)

[2] P. Bordet et al., *Crystal Growth and Design* 16, 4547 (2016)

[3] P. Martinetto et al., *Crystal Growth & Design* 17, 6111 (2017)

Thursday 5 July morning - 10:00/11:00

Parallel Session 4  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES IV**  
Chair: L. Battezzati

**ID-444 (invited)****Indirect assessment of sample temperature in plasma environment during electric discharge assisted mechanical milling**

*A. Calka, M. Wyszomirska, D. Wexle*

*University of Wollongong*

Electric discharge assisted mechanical milling (EDAMM) [1] is a new materials processing technique which combines the attributes of conventional mechanical milling with all effects generated by electric discharges. It is demonstrated that EDAMM can be used to process and synthesize a range of functional materials in a matter of minutes, rather than days.

Over the last few years we have used this method to create rapid reduction and replacement reactions, to rapidly synthesize complex oxides, and ultrahard materials, also to study hydrogen metal interactions. On the base of experiments done so far we have fairly good understanding of the EDAMM process parameters such as voltage – current, DC and AC discharge characteristics, cell vibration frequency and type of atmosphere. However, there is still difficult to assess the temperature of samples processed in plasma discharge environment. In the case of highly dynamic nature of the EDAMM the measurement of sample temperature is not possible using conventional methods.

The aim of this study is to develop a fundamental understanding of the EDAMM processing temperatures and process conditions that may affect the sample temperature.

This was done through processing of a variety of materials which exhibit a phase transformation or polymorphic transformation in a known temperature.

A series of experiments using metal (Al, Mn, Ti, Cr), non-metals (Si, C) and oxide ( $\text{TiO}_2$ ,  $\text{BaTiO}_3$ ) starting materials was designed to observe the minimum and maximum temperatures during the EDAMM processing using stainless steel ball electrode in Ar atmosphere. The minimum processing temperature in these conditions was determined according to the Al melting point and Mn polymorphic transformation. Ti+Cr and BaO+ $\text{TiO}_2$  powders were mixed in the stoichiometric ratios to form  $\text{TiCr}_2$  and  $\text{BaTiO}_3$ , respectively, to determine the intermediate processing temperature. The maximum processing temperature determination was done using Si+C powders to form high temperature SiC compound.



Further investigation of the cubic ↔ hexagonal BaTiO<sub>3</sub> polymorphic transformation was used to determine the influence of ball electrode TaC coating on the processing temperature and reaction sequence in intermediate temperatures range. The transformations of the crystal structures were investigated using X-ray diffraction (XRD), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM).

[1] A. Calka and D. Wexler, Nature 419, 147 (2002)

## ID-353

**The structure of “ $V_4Nb_{18}O_{55}$ ” metastable ternary oxide compound prepared by extended ball milling of  $V_2O_5$  and  $Nb_2O_5$  powders and thermal treatment.**

*S. Enzo<sup>1</sup>, A. Iacomini<sup>1</sup>, N. Senes<sup>1</sup>, A. Santoru<sup>2</sup>, S. Garroni<sup>3</sup>, C. Pistidda<sup>2</sup>, G. Mulas<sup>1</sup>*

<sup>1</sup> *University of Sassari*

<sup>2</sup> *Helmholtz-Zentrum Geesthacht GmbH*

<sup>3</sup> *University of Burgos*

The phase diagram of the  $V_2O_5$  -  $Nb_2O_5$  quasi-binary system was investigated more than 50 years ago. In spite of several attracting properties of such mixed transition metal oxides for a wide diversity of electronic devices, due to their semiconducting, superconducting and ionic conducting properties as well as in catalysis and for hydrogen storage, the correct structure attribution of possibly metastable compounds seems to have proceeded with difficulty. This may be due especially for Nb-rich compositions because of the polymorphism typical of  $Nb_2O_5$  oxides and of the synthesis processing adopted. The latter seems strictly related to soft-chemistry approaches like sol-gel, co-precipitation or alternatively thermal decomposition of freeze-dried precursors affording an amorphous mixture of the two metal oxides that need further annealing for subsequent crystallization.

Only recently, after a very long debate, the structure of the compound quoted as “ $V_4Nb_{18}O_{55}$ ” has received a solution in terms of the space group Cmmm inspired by tetragonal tungsten bronze (TTB)-type structure which has high potential for ionic intercalation. However, inspection of the atomic coordinates from the proposed CIF file suggests unreasonable density and/or interatomic distance distribution for the nearest neighbours.

On the other hand, the availability of methods for “ab-initio” structural solution and final refinement starting from powder pattern data should permit to ascertain with good degree of reliability the structure of such new phases in terms of space group, atomic coordinates and density.

We have used a simulated annealing programme for structure solution (Endeavour) to account for our powder X-ray diffraction data obtained after synthesis of  $V_2O_5$ : $XNb_2O_5$  powders ( $X = 1, 2, 3$  and  $5$ ) by ball milling, followed by thermal annealing at temperatures below  $700\text{ }^\circ\text{C}$ . Our results suggest that so called “ $V_4Nb_{18}O_{55}$ ” may be orthorhombic, lattice parameters  $a = 3.965\text{ }\text{\AA}$ ;  $b = 17.395\text{ }\text{\AA}$   $c = 17.742\text{ }\text{\AA}$  of stoichiometry  $V_4Nb_{20}O_{30}$ . Space group  $Amm2$  (n. 38), Pearson symbol  $oA84$ , density =  $4.10\text{ g/cm}^3$ .

In this structure, while niobium atoms may be four, five and six-fold coordinated by oxygen atoms, the vanadium atoms are six-fold or seven-fold coordinated, respectively.

**ID-47****In-situ dispersed La oxides of Al6061 composites by mechanical alloying**

C-L Chen, C-H Lin

*Department of Materials Science and Engineering, National Dong Hwa University, Hualien 97401, Taiwan*

Aluminium-based metal matrix composites (MMCs) are ideal materials for structural applications due to their high strength to weight ratio. In this study, addition of the rare earth element-Lanthanum in Al<sub>6061</sub> alloys as in-situ La<sub>2</sub>O<sub>3</sub> particles fabricated by mechanical alloying was investigated. The result shows that an increase of La contents can changes morphology of synthesized powders and has significant influence on microstructure uniformity, hardness, densification, and ductility of the materials. The results also suggest that the La-rich oxides and complex La-Si and AlFeSi compounds can be formed during ball milling and subsequent sintering processes.

Thursday 5 July morning - 11:30/13:00

Parallel Session 1  
**NANOSTRUCTURED MATERIALS X**  
J.M. Greneche

ID-425

**In-situ compression of hollow BN nanoparticles in a high-resolution transmission electron microscope***K. Firestein<sup>1</sup>, A. Kovalskii<sup>2</sup>, A. Bondarev<sup>2</sup>, D. Shtansky<sup>2</sup>, D. Golberg<sup>1</sup>*

<sup>1</sup> School of Chemistry, Physics and Mechanical Engineering, Queensland University of Technology (QUT), Brisbane, Queensland 4000, Australia.

<sup>2</sup> National University of Science and Technology (NUST) "MISiS"

Boron nitride (BN) forms a large variety of nanostructures such as straight, cylindrical, faceted and bamboo-like nanotubes, graphene-like nanosheets and nanoplates, nanospheres and nanocones. BN nanostructures attract much attention both as thin films and reinforced components of composite materials due to their exceptional mechanical, physical and chemical properties. Extremely high values of strength and elastic modulus have been confirmed by experimental and theoretical studies for BN nanotubes, nanoribbons, and two-dimensional (2D) BN nanosheets. However, there is no information about mechanical properties of another morphological type of BN structure – spherical hollow BN nanoparticles. But these nanoparticles can be widely used as catalyst supports, nanocarriers for drug-delivery, additives for liquid lubricants, reinforcing phase in metal matrix composites, and UV-shielding materials.

In present work hollow, spherical nanoparticles with an average size of 100-250 nm were synthesized via boron oxide-assisted chemical vapour deposition technique. Mechanical properties of BN nanoparticles were studied using in situ compression in a high-resolution transmission electron microscope. Compression of individual BN nanoparticle were performed in a JEM 2100 microscope (JEOL) using a depth-sensing PI 95 TEM Picoindenter (Hysitron). For in situ testing, BN were deposited onto the wedge located on the surface of Si substrate using nanoparticles suspension in isopropanol. During deformation, force-time and force-displacement curves were recorded. The compression tests were carried out using a diamond flat end conical tip with 1  $\mu\text{m}$  diameter of the top circle. Samples were loaded and unloaded at a rate of 2.5 nm per second.

As a result, it was found that synthesized materials had displayed high mechanical stiffness and a large value of elastic recovery. This enables the hollow BNNPs to exhibit considerably large cyclic deformation (up to 30% of the sphere's original external diameter) and to accumulate plastic deformation of approximately 30% of the total compression strain.

ID-188

**Amorphous TiAl freestanding thin films studied by in-situ TEM**C. Ebner<sup>1</sup>, R. Sarkar<sup>2</sup>, J. Rajagopalan<sup>2</sup>, C. Rentenberger<sup>1</sup><sup>1</sup>University of Vienna, Faculty of Physics, Physics of Nanostructured Materials<sup>2</sup>Arizona State University, Department of Materials Science and Engineering, School for Engineering of Matter, Transport and Energy

Amorphous materials show good mechanical, physical and chemical properties leading to their increased scientific and engineering importance in the last decades. The mechanical behavior of amorphous materials is directly connected to the atomic structure, but due to the lack of long-range order in amorphous structures this interrelation is not easily accessible even for the case of elastic deformation. Nevertheless, it has been shown that atomic-level elastic strain can be measured from X-ray scattering images. Recently, we demonstrated the applicability of this experimental approach to electron scattering of micro/nano-scaled thin films in the transmission electron microscope (TEM) by analyzing distorted selected area electron diffraction (SAD) images [1]. We applied this method to study the structural and mechanical response of amorphous TiAl thin films strained within the elastic regime. Hitherto, we focused (i) on the elastic stress-strain response to calculate Young's modulus and Poisson's ratio, (ii) on the local atomic-level elastic strain as a function of sample position (strain mapping), (iii) on uncoupling anelastic and elastic strain [2] and (iv) on the time dependent viscoelastic strain response.

In-situ tensile deformation was carried out on freestanding amorphous TiAl thin films with a Philips straining holder in a conventional TEM. The thin film deposited by magnetron sputtering of pure Ti and Al on a MEMS device was prepared freestanding by standard masking and etching techniques. SAD patterns were acquired as function of stress, time and sample position. The distortion of the SAD pattern occurring under stress was measured and compared to the SAD pattern of the unloaded state. The change of the ring distortion at different stress levels can be tracked and used to calculate the corresponding 2D strain tensor. In the case of time dependent strain response a clear impact of the electron beam could be revealed. To simulate the amorphous structure and get information on the changes by the electron beam classical molecular dynamics calculations were used.

Financial support by the Austrian Science Fund (FWF): I1309 and the National Science Foundation (NSF) Grants CMMI 1400505 and DMR 1454109 is acknowledged.

[1] C. Ebner, R. Sarkar, J. Rajagopalan, C. Rentenberger, *Ultramicroscopy* 165, 51 (2016).

[2] R. Sarkar, C. Ebner, E. Izadi, C. Rentenberger, J. Rajagopalan, *Mater. Res. Lett.* 5, 135 (2016).

## ID-390

**Effect of biaxial cyclic severe deformation on structure and properties of Ti-Ni alloys**

*V. Komarov<sup>1</sup>, I. Khmelevskaya<sup>1</sup>, S. Prokoshkin<sup>1</sup>, M. Isaenkova<sup>2</sup>, M. Zaripova<sup>2</sup>, R. Kawalla<sup>3</sup>, G. Korpala<sup>3</sup>*

<sup>1</sup> National University of Science and Technology "MISIS"

<sup>2</sup> National Research Nuclear University MEPhI

<sup>3</sup> TU Bergakademie Freiberg

The severe plastic deformation (SPD) is one of the most effective methods to improve the functional properties of Ti-Ni shape memory alloys (SMA). It allows formation of an ultrafinegrained structure which is characterized by the best combination of functional properties. Development of SPD methods is concluded in a searching for thermomechanical procedures which allow producing bulk samples with a nanocrystalline structure. The "MaxStrain" (MS) module for multi-axial deformation which is a part of the "Gleeble" system for physical modeling of thermomechanical processes allows performing SPD of the material under isothermal conditions with precise control of temperature in the deformation zone and strain rate, and simulating the rolling and forging processes. The formation of a structure close to the nanocrystalline (NC) in equiatomic Ti-Ni alloys by the use of MSdeformation has been shown previously. However, there was no information about morphological features of the structure and crystallographic texture development in Ti-Ni SMA.

In this work, the MS-deformation was carried out under the most severe conditions, i.e. until the appearance of the first cracks. For Ti-50.0 at.% Ni it happened at  $T=250^{\circ}\text{C}$ ,  $e=11$ ; for Ti-50.9 at.% Ni at  $T=330^{\circ}\text{C}$ ,  $e=9.5$ . The early destruction of the alloy with increased nickel content is due to the presence of  $\text{Ti}_3\text{Ni}_4$  phase particles that reduces the plasticity.

The kinetics of martensitic transformations were studied by DSC method, and the structure and texture features using X-ray diffractometry and TEM (from three mutually perpendicular sides). The maximum completely recoverable strain was determined by a thermomechanical method using a bending mode for strain inducing.

MS-deformation ( $T=250^{\circ}\text{C}$ ,  $e=11$ ) of Ti-50.0 at.% Ni leads to the formation of a NC grain/subgrain structure with an average grain/subgrain size of  $55\pm 10$  nm, which has not been obtained in bulk samples of Ti-Ni SMA until now and provides an obvious advantage in the completely recoverable strain (9.6%) as compared to a reference treatment (2.5%). The texture and anisotropy of the structure after the most severe the MS-deformation modes are weakened and disappear.

The mechanical behavior and structure formation of the Ti-50.9 at.% Ni alloy differs from Ti-50.0 at.% Ni due to the effect of the  $\text{Ti}_3\text{Ni}_4$  phase particles. The use of this alloy after MS-deformation requires the use of annealing.

ID-409

**Interface polarized charge transfer in half-metal/semiconductors nanocomposites***O. Pana, M. Stefan, M-L Soran, A. Popa, S. Gutoiu, D. Toloman, S. Macavei, C. Leostean**National Institute for Research and Development of Isotopic and Molecular Technologies*

Different types of magnetic nanoparticles composites can be designed as multifunctional platforms with controllable magnetic properties, thus being able to facilitate their use in different applications. Moreover, the interface interactions between different components can greatly improve the performance of the multi-components system and even generate new synergetic properties. At the interface between a metal and a semiconductor the work functions should be equalized producing a charge transfer across the interface. When a half-metal (HM) ferromagnetic material (FM) is interfaced with a semiconductor, at nano scale, the charge transfer is spin polarized. A common HM-semiconductor Bloch wave, with coherent spin polarization, should be formed. Depending on the HM Fermi level position, the charge/spin transfer goes from the HM into the semiconductor or in the reverse way. In the former case localized states should be available in the semiconductor band gap. Here the spin polarized states will lose their coherence which in turn leads to the reduction of the saturation magnetization on the HM side. In the second case the charge transfer goes into CB states above the HM Fermi level. It should be in accordance to the spin polarization required here. Spin polarized states will induce, via indirect exchange, a carrier-mediated magnetism on the semi-conductor side as given by RKKY calculations. In addition the coercivity of hard HM FM is reduced through the exchange coupling with the magnetic semiconductor. The process may be understood within the Preisach model and its improvements. For exemplification and discussion two types of HM magnetic nanoparticles (NP) as magnetite and FePt (L10) alloy were coated with semiconductors like ZnS, TiO<sub>2</sub>, SnO<sub>2</sub> and poly(3 hexylthiophene) (P<sub>3</sub>HT). By ZnS coating of Fe<sub>3</sub>O<sub>4</sub> NP the saturation magnetization significantly increases while TiO<sub>2</sub> coating gives a reversed process. In case of FePt NP coated with P<sub>3</sub>HT a significant reduction of the coercivity is observed. Both types of charge/spin transfer may coexist as in the special case of superparamagnetic HM Fe<sub>3</sub>O<sub>4</sub> nanoparticles covered with SnO<sub>2</sub> nano-dots. Here the charge/spin transfer involves, besides the semiconductor gap states also its filled conduction band states.

Financial support from the Romanian Ministry of Research and Innovation, Core Prog. PN18-03 02 03 is gratefully acknowledged.



ID-419

**Microstructure, hardness and their thermal stability in electrodeposited nanocrystalline Ni layers with different Mo content***G. Kapoor<sup>1</sup>, L. Peter<sup>2</sup>, N.Q. Chinh<sup>1</sup>, J. Gubicza<sup>1</sup>*<sup>1</sup> *Eötvös Loránd University*<sup>2</sup> *Hungarian Academy of Sciences, Budapest, Hungary*

An investigation was conducted to examine the influence of Mo addition on the microstructure and hardness of electrodeposited nanocrystalline nickel (Ni) films. The electrodeposited layers were prepared by a galvanostatic electrolysis at room temperature, with a constant current density and pH value. The chemical composition of these layers was determined by energy-dispersive spectroscopy (EDS). Differential scanning calorimetry (DSC) was used to investigate the thermal stability of the phase composition and the microstructure. The Ni-Mo layers with low and high Mo concentrations were investigated by X-ray line profile analysis (XLPA) before and after the exothermic DSC peak to determine the microstructural parameters such as the crystallite size, the dislocation density and the twin fault probability. In addition, the influence of the DSC heat treatment on hardness was also investigated by nanoindentation. The results show that the thermal stability of Ni-Mo films was strongly improved by the increase of the Mo content. A comparative study was made with a previous research on bulk ultrafine-grained Ni-Mo materials with similar compositions but processed by severe plastic deformation.

ID-326

**On precipitation of icosahedral nanoquasicrystalline phase in Hf-Cu-Ni amorphous alloys***A. Khond<sup>1</sup>, A. Babu<sup>2</sup>, B. Majumdar<sup>2</sup>, J. Bhatt<sup>1</sup>, A.K. Srivastav<sup>1</sup>**<sup>1</sup> Department of Metallurgical and Materials Engineering, Visvesvaraya National Institute of Technology, Nagpur (India)**<sup>2</sup> Defence Metallurgical Research Laboratory, Kanchanbagh, Hyderabad (India)*

In the present work, the role of intermediate icosahedral quasicrystalline phase on crystallization behaviour of Hf-Cu-Ni amorphous alloys was investigated.  $\text{Hf}_{64}\text{Cu}_{18}\text{Ni}_{18}$  amorphous ribbon was prepared by melt-spinning technique. Crystallization pathway of the ribbon was studied by X-ray diffraction (XRD), differential scanning calorimetry (DSC) and transmission electron microscopy (TEM). Stable  $\text{Hf}_2\text{Cu}$  and  $\text{Hf}_2\text{Ni}$  crystalline phases were formed during the crystallization of amorphous ribbon. Crystallization proceeds with the appearance of icosahedral quasicrystalline phase followed by the stable  $\text{Hf}_2(\text{Cu}, \text{Ni})$  phases. TEM analysis confirms the intermediate metastable icosahedral quasicrystalline phase in annealed amorphous ribbon before the evolution of stable  $\text{Hf}_2(\text{Cu}, \text{Ni})$  phases.

Thursday 5 July morning - 11:30/13:00

Parallel Session 2  
**METALLIC GLASSES X**  
S. Hosokawa

**ID-365****Cryogenic thermal and mechanical processing of Ti-Ni-Cu-Zr based crystal/glassy alloys**

*J. Jiang<sup>1</sup>, D. Louzguine-Luzgin<sup>2</sup>, H. Kato<sup>1</sup>*

<sup>1</sup> *Tohoku University, IMR*

<sup>2</sup> *Tohoku University, WPI-AIMR*

Ti-Ni-Cu-Zr-Co-Y system crystal/glassy dual-phase materials containing a glassy phase and a crystalline phase studied here exhibit a good combination of high strength and plasticity. They undergo a martensitic transformation during deformation and exhibit the superelastic behavior and excellent mechanical properties: mechanical strength up to 2.5 GPa and plasticity of more than 20 %. Mechanical characteristics of the alloys revealed three deformation stages, which include a martensitic transformation and “superelastic” type effect. Structural changes induced by deformation during the loading/unloading cycles cause changes in the stress-strain hysteresis, i.e. increasing the residual strain and decreasing the critical stress for martensite transformation. The amorphous phase acts as the barrier for dislocation slip and austenite-martensite phase transition during the superelastic cycling and reduces residual strain compared to cP2 TiNi crystalline sample. The Ti-Ni-Cu-Zr-Co-Y composite was also treated by the thermal processing to improve the mechanical properties. Considering possible rejuvenation of amorphous phase by thermal cycling between room and the liquid nitrogen temperature (77 K), we found that the fatigue could be suppressed by the subsequent cryogenic thermal cycling. The results of compressive tests indicate that the martensitic transformation inducing stress, which is decreased upon the superelastic loading cycles, is recovered on the cryogenic thermal treatment.

**ID-457****Two-way structural tuning of the ordering states in a metallic glass***H. Lou, Q. Zeng**Center for High Pressure Science and Technology Advanced Research*

Metallic glasses, without the strict constraints of well-defined crystalline symmetry and large energy barriers separating different states in crystals, are expected to have quite flexible and tunable structures. Effectively modulating the structure of metallic glasses, however, is rather difficult. Here, using complementary in situ synchrotron X-ray techniques, we reveal a thermal-driven structural ordering in a Ce-based metallic glass, and a reverse disordering process via a pressure-induced rejuvenation between two polyamorphous states with distinct structural order characteristics. Our findings demonstrate the feasibility of a two-way structural tuning of amorphous states in terms of ordering and disordering far beyond the nearest-neighbor shells with the combination of temperature and pressure. It extends accessible metallic glass states to unexplored phase regions, introducing new avenues for the development of novel metallic glasses.

## ID-218

**Characterization of the stress-temperature-time relaxation spectrum of metallic glasses***E. Pineda<sup>1</sup>, F. Yang<sup>2</sup>*<sup>1</sup> *Departament de Física, Universitat Politècnica de Catalunya*<sup>2</sup> *Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt (DLR)*

The mechanical and rheological properties of metallic glass-forming alloys are directly related to their relaxation spectrum. Together with the main structural  $\alpha$ -relaxation, metallic glass formers show secondary relaxations of various kinds. Some of these secondary processes have been associated to the Johari-Goldstein relaxation but also to other origins [1], the activation of these processes depends on temperature as well as on the applied stress level [2]. In this work, stress relaxation, creep and mechanical spectroscopy experiments have been performed on vitreloy4, a well-known, high glass-forming-ability alloy, with the purpose of obtaining an unprecedentedly detailed stress-temperature-time relaxation map. The characterization covers a wide range of temperatures, from room temperature ( $\sim 0.5T_g$ ) to  $1.15T_g$ , and times from  $10^4$  to  $10^{-3}$  s. The stress domain was explored by stress relaxation and mechanical spectroscopy applying deformations going from 0.005el to 0.5el (el $\sim$ 2% the elastic limit typical of metallic glasses). Furthermore, below  $T_g$ , in the glassy state, the relaxation map was obtained for different fictive temperatures.

The observed relaxation processes were classified in terms of their anelastic (reversible) or viscous-like nature, with characteristic times showing very different temperature dependences. The relative contribution to stress relaxation of each type of process was found to be dependent on both temperature and stress level. In addition to the detailed description of the stress-temperature-time relaxation map of vitreloy4, we will interpret the results in terms of the current metallic-glass relaxation models and the relaxation spectrum obtained in other metallic glasses [3]. Finally, we will discuss what processes are expected to be universal of all glass formers and which are characteristic of certain metallic systems.

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[2] E. Pineda et al., *Acta Mater.* 61, 3002 (2013)

[3] C. Liu et al., *J. Alloys Compd.* 643 S17 (2015); C. Liu et al., *J. Phys. Chem. B* 120, 2838–44 (2016)

ID-184

**Evaluating metallic glasses as research areas using bibliometric maps and indicators***D.H. Milanez<sup>1</sup>, E.C.M. Noyons<sup>2</sup>, W.J. Botta<sup>1</sup>, C.S. Kiminami<sup>1</sup>*<sup>1</sup> *Federal University of São Carlos*<sup>2</sup> *Leiden University*

Amorphous/glassy metals (AGM) have been subject of deep scientific investigation due to its interesting chemical, magnetic and mechanical properties. Efforts have been expended in producing and characterizing AGM in view to apply them in magnetic components, electronic products, medical devices, sporting goods and coatings. Nonetheless, less attention has been paid to examine the impact of AGM as a research area. This study aims at assessing AGM using a Publication-level Classification System (PLCS) developed by the Centre for Science and Technology Research, Leiden University, the Netherlands. The PLCS is based on clustering publications indexed in Web of Science using citation as the main criteria. The analyses entail citation and collaboration maps, impact indicators and text mining approaches to assess research areas, countries, research institutions and hot topics on AGM. The characterization involved seeking all research areas containing at least one publication about AGM using a term-based search expression. A total of 538 research areas were identified, but only one accounted for 70% of the total number publication retrieved – considered to be the core area, while 534 research areas represented less than 1%. An analysis of publications from the core area confirms that it contains AGM publications only. The top relevant research areas associated to the sample includes magnetic properties, surface tension and viscosity of liquid metals, quasicrystals, gas atomization, and high entropy alloys. The text mining analysis of AGM core area pointed out that mechanical mechanisms and properties, topics related to glass formation ability, coatings and corrosion/wear resistance are hot topics. Although China, USA and Japan headed the publication ranking, Germany has been central in the citation map. Tohoku University occupies a central spot in the collaboration map, while Johns Hopkins University, University of Cambridge and California Institute of Technology have the highest impact in the AGM researchers' community. The Korean Sejong University, Pohang University of S&T and Korea Institute of S&T, as well as the American Caltech, had the highest number of publications co-authored with industry partners. This might indicate that the probability of technological transfer from these institutions is higher than from other players. We conclude that the evaluating approached adopted in this study was useful to characterise the AGM as a research area.

## ID-342

**Transition from decagonal to icosahedral structure resulted by Co to Fe substitution in Al-Cu-Co-Fe alloys**

*D. Shulyatev<sup>1</sup>, M. Klyeva<sup>1</sup>, N. Andreev<sup>1</sup>, N. Tabachkova<sup>1</sup>, A. Suslov<sup>2</sup>, T. Sviridova<sup>1</sup>*

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<sup>2</sup> National High Magnetic Field Laboratory, Tallahassee, Florida 32310

We developed a conceptual AlCu(Fe+Co) phase diagram and studied structural transformation when cobalt is substituted by iron. Large (mm-size) single-grain samples with different Co/Fe ratio were obtained by an original two-step cooling process consisting of fast cooling of a melt with a specific composition into a single quasicrystalline phase region followed by slow cooling of the obtained mass to room temperature. Structural analysis revealed a quasicrystalline structure with decagonal symmetry in the low-iron-content specimens and icosahedral symmetry in the high-iron-content samples. Temperature dependencies of the electrical resistance in the range of 1.4 K - 300 K were measured by the four-probe method on oriented samples which were shaped as rectangular parallelepipeds. The resistivity behavior of low-iron-content samples is typical for anisotropic decagonal quasicrystals while in the high-iron-content samples it is close to  $\rho(T)$  in ternary icosahedral i-Al- Cu-Fe.

This work was supported by the Ministry of Education and Science of the Russian Federation in the frame work of Increase Competitiveness Program of NUST MISIS (K2-2017-080) and grant RFBR No16-02-01004 A. NHMFL is supported by National Science Foundation Cooperative Agreement No. DMR-1157490 and the State of Florida.



ID-282

**Crystallization of Cu-Zr thin film metallic glass via femtosecond laser heating**

*J. Antonowicz<sup>1</sup>, R. Sobierajski<sup>2</sup>, P. Zalden<sup>3</sup>, K. Sokolowski-Tinten<sup>4</sup>, A. Pietnoczka<sup>1</sup>, M. Chaika<sup>2</sup>, P. Dłużewski<sup>2</sup>, M.T. Klepka<sup>2</sup>, D. Klinger<sup>2</sup>, R. Minikayev<sup>2</sup>, K. Fronc<sup>2</sup>, M. Chojnacki<sup>2</sup>, O. Magnussen<sup>5</sup>, Ch. Lemke, K. Georgarakis<sup>6</sup>, L. Greer<sup>7</sup>, U. Ruett<sup>8</sup>, K. Perumal<sup>8</sup>, J. Varias<sup>5</sup>, B. Murphy<sup>5</sup>*

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In this work we employ ultra-fast heating by femtosecond laser pulses to study crystallization kinetics of thin film of  $\text{Cu}_{65}\text{Zr}_{35}$  metallic glass by X-ray diffraction (XRD) at the synchrotron light source. The essential feature of our approach is an ultra-fast heating ( $10^{14}$  K/s) by femtosecond optical excitation followed by extremely rapid cooling ( $10^{12}$  K/s) by heat dissipation into the film substrate. This unique technique allows to precisely control transformation conditions and to quantify crystallization kinetics over a wide range of effective crystallization temperatures. In our experiment, we have acquired consecutive diffraction snapshots at the frozen-in intermediate stages of transformation. This way we could follow nucleation and growth of the crystalline phases formed after repetitive laser heating of the metallic glass thin film. The integrated 2D XRD patterns taken at different stages of transformation were deconvoluted into a broad amorphous “halo” and sharp Bragg peaks of the crystalline phases. From the XRD data we evaluated the time-dependent crystalline volume fraction and by employing Scherrer equation estimated the crystal growth rate. By combining the XRD results with scanning and transmission electron microscopy data we found that the devitrification process of  $\text{Cu}_{65}\text{Zr}_{35}$  glassy film is initiated by surface oxidation which proceeds by ultra-fast (100 m/s) growth of a uniform layer of a high-temperature cubic  $\text{ZrO}_2$  phase. Simultaneously, signatures of the amorphous phase separation initiated by optical excitation and were observed in the glassy film. Our results indicate that due to formation of zirconium oxide, the metallic glass film becomes enriched in copper and crystallizes as soon as its average composition reaches the boundary of glass formation range located at about 30% of Zr.

Thursday 5 July morning - 11:30/13:00

Parallel Session 3  
**PHASE TRANSFORMATION II**  
M. Kaufman

## ID-123

**Structure and magnetic properties of Fe-Ga alloys doped by Tb**

*V. Palacheva*<sup>1</sup>, *I. Bobrikov*<sup>2</sup>, *A. Balagurov*<sup>2</sup>, *V. Cheverikin*<sup>1</sup>, *I.S. Golovin*<sup>1</sup>

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<sup>2</sup> Joint Institute for Nuclear Research

This research deals with the Tb dependence of magnetostriction and magnetic properties in  $\text{Fe}_{19}\text{Ga}_x\text{Tb}$  ( $x = 0-0.37$  at %) and  $\text{Fe}_{27.4}\text{Ga}_x\text{Tb}$  ( $x = 0-0.5$  at %) alloys. Addition of Tb improves the saturation magnetostriction in the  $\text{Fe}_{19}\text{Ga}_x\text{Tb}$  and  $\text{Fe}_{27.4}\text{Ga}_x\text{Tb}$  alloys. The magnetic permeability and magnetocrystalline anisotropy constant are also increased by the addition of Tb.

Ga and Tb enriched phase (up to 7 at % Tb and 41 at % Ga) is observed at the grain boundaries and inside the interdendritic regions after direct solidification. Chemical compositions of all phases in the alloys are analysed and the solubility limit of Tb in studied Fe-Ga is estimated to be  $<0.15$  at %. Study of alloys microstructure shows two phase (D03 and Tb+Ga-rich phase) structure in  $\text{Fe}_{19}\text{Ga-Tb}$  and three phase (D03, L12 and Tb+Ga-rich phase) in  $\text{Fe}_{27.4}\text{Ga-Tb}$  type alloys.

Several aspects of the formation of functional Fe-Ga alloys are considered: the mechanism of phase transition from a metastable ordered bcc-derivative phase to an equilibrium fcc-derivative ordered phase, the nature of corresponding anelastic effects, the usage of isothermal annealing for the formation of an intrinsic composite microstructure with a different ratio between the bcc-derivative metastable and fcc-derivative equilibrium phases that have different magnetic properties, and the effect of an additional doping by Tb to stabilize bcc-derivative phases with high positive values of magnetostriction. In situ neutron diffraction, measurements of magnetostriction and magnetization, mechanical spectroscopy were applied to achieve the goals of this study using  $\text{Fe}_{27}\text{Ga}$  type alloys. The reversible order – disorder phase transition of  $\text{D03} \leftrightarrow \text{A2}$  leads to a transient anelastic effect at  $\approx 555$  C° and  $\approx 520$  C° respectively upon heating and cooling of the  $\text{Fe}_{19}\text{Ga-Tb}$  alloy was supported by neutron diffraction and vibrating sample magnetometry tests.

ID-452

**Preparation and characterization of novel Heusler type magnetic microwires***M. Ipatov<sup>1</sup>, V. Zhukova<sup>1</sup>, P. Corte-Leon<sup>1</sup>, T. Ryba<sup>2</sup>, R. Varga<sup>2</sup>, J. Gonzalez<sup>1</sup>, A. Zhukov<sup>1</sup>*<sup>1</sup> Dept. Phys. Mater., University of Basque Country, UPV/EHU San Sebastián 20018, Spain<sup>2</sup> Inst. Phys., Fac. Sci., UPJS, Park Angelinum 9, 041 54 Kosice, Slovakia

Heusler alloys known since 1903, recently attracted special attention owing to the discovery of half-metallic ferromagnetism and the observation of the shape memory effect in some of Heusler alloys. The Heusler alloys therefore are proposed for prospective applications in magnetic cooling, actuators and energy harvesting [1,2]. The functionality of the Heusler alloys can be considerably improved by miniaturization of Heusler-type materials [2,3]. As an example, for magnetic cooling the enhancement of the surface-to-volume ratio allowing for increase of the heat exchange rate is essential. Consequently, a few attempts have recently been taken to prepare Heusler alloys either in thin wires or thin films [4,5].

Here we present our experimental results on the preparation and characterization of Co<sub>2</sub>FeSi glass-coated microwires. The XRD diffractogram was obtained in a coupled Theta- 2 Theta geometry with Cu K $\alpha$  radiation. The magnetic properties were measured in temperature range 5-400 K by vibrating sample magnetometer. In the as-cast state, the RXD diffractogram shows that the sample is mainly amorphous with a small crystalline part. Further we performed a temperature annealing at 873 K during 1 and 6 hours. After annealing the crystalline content is increasing, though a complete crystallization is not archived.

The temperature dependencies M vs T were measured with applied axial magnetic field on cooling ( $F_C$ ) and heating ( $F_H$ ). The  $F_C$  and  $F_H$  curves generically coincide except at the lowest measured field of 50 Oe, some mismatch is observed. This could mean a phase transition. Also the slope of the temperature dependencies dM/dT vs T is different for different fields. The hysteresis loops are rather square ones with coercivity about 70 Oe at room temperature. A reducing of the coercivity field is observed at temperature below 55 K. Summarizing we demonstrated that the Taylor-Ulitovsky technique is suitable for preparation of Co<sub>2</sub>FeSi glass-coated microwires.

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ID-301

**Current annealing crystallization of Co-rich amorphous microwires for miniature hard-magnet applications**

M. Nematov<sup>1</sup>, A. Adam<sup>1</sup>, L. Panina<sup>1</sup>, I. Baraban<sup>2</sup>, A. Morchenko<sup>1</sup>, V. Korovushkin<sup>1</sup>, V. Rodionova<sup>2</sup>

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Amorphous microwires of Co-rich compositions are known as excellent soft-magnetic materials exhibiting a number of outstanding effects such as magnetic bistability, giant magnetoimpedance and stress-impedance which are used in sensing and smart materials applications. For all these applications, the use of hard magnetic elements of similar dimensions together with the sensing wire can provide additional functionality. Hard magnetic microwires are also of interest for bio-medical applications as they could be implanted within a targeted area of tissue or blood vessel to control the migration of living cells and targeted drug delivery. However, a preparation of hard magnetic microwires is a difficult task. The crystallization process strongly affects the wire magnetic properties. In the case of gradual heating with a constant temperature changing rate the crystallization proceeds in two main stages in the temperature range of 500-700 and results in deterioration of soft magnetic properties. The magnetic anisotropy increases but typically the coercivity does not exceed 1-2 kA/m. Utilizing specific heating-exposure-cooling cycles the coercivity can be further increased up to 30 kA/m but the remanence magnetization remains small. A process of directional crystallization was proposed in [2] to enhance the hard magnetic properties. In this case, crystallization proceeds through a number of metastable states which makes it difficult to control the resulting microstructure and magnetic parameters. In the present paper, current annealing is proposed as an alternating crystallization technique to produce hard magnetic microwires. Depending on the annealing time (30-60 minutes) the coercivity of  $\text{Co}_{71}\text{Fe}_5\text{B}_{11}\text{Si}_{10}\text{Cr}_3$  microwires was increased up to 50 kA/m with the remanence to saturation ratio of about 75%. Structural characteristics of samples before and after annealing were investigated by using XRD, SEM and TEM. The formation of needle-shaped crystals of Co and their arrangements by circular magnetic field may be responsible for giant increase in coercivity. Therefore, we put forward a novel technique for micro-magnet fabrication.

Refs:

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ID-481

**Electronic transport properties as a tool to characterize phases of alloys and their changes***N. Fazel, F. Gasser, J-G Gasser**Université de Lorraine LCP-A2MC*

By electronic transport properties, one generally understands electrical and thermal conductivity and Absolute Thermoelectric Power (ATP). These properties are a very accurate method to characterize the phase in which the system is, since we can measure the electrical resistivity with a very high resolution (typically 1/10000). Roughly, one can obtain the same information's than DSC, but the great advantage of electronic transport is that phase changes can be followed even at constant temperature (ageing) during a very long time. Typically, we did a 1000 hours (two month) test at constant temperature. We realized an automatic device, driven by a LabView program, to measure electrical resistivity and ATP between room temperature and 1200° Celsius (a). In its present version, the program can be used between 25K and 1600K and it can, if necessary, be extended in the range from 4K to 2041K. We tested the device on  $\text{Ni}_{36.5}\text{Pd}_{36.5}\text{P}_{27}$  (b) and on  $\text{Ni}_{33.3}\text{Zr}_{66.7}$  (c) metallic glasses.

In this work, we present new experimental results on different amorphous materials. We follow the recrystallization of the amorphous alloy but also its time transformation during several weeks, probably by the increase of the size of the grains until the system no more evolves. We also present other experimental results on shape memory alloys reversible transformation and on the construction of TTT diagrams of titanium.

Electronic transport is an accurate method to control micro-structural transformations due to ageing, tempering, annealing, segregation, austenitizing, precipitation, decomposition of solid solutions, texturation and to follow the effects of mechanical stress and why not to understand resistivity and thermopower of alloys and pseudoalloys.

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c) B. Smili, A. Messaoud, W. Bouchelaghem, L. Abadlia, N. Fazel, A. Benmoussa, I. Kaban, F. Gasser, J.G. Gasser *JNCS* 481 (2018) 352

ID-432

## Phase stabilisation and stress evolution in tantalum thin films deposited by magnetron sputtering

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<sup>2</sup> ENSMA, Département Physique et Mécanique des Matériaux

Over the past decades, great attention has been devoted to the sputtering growth of Ta thin films, as possible applications include protective coatings, X-ray optics or microelectronics, e.g. as diffusion barriers in integrated circuits with copper interconnects. It is commonly observed that the metastable tetragonal  $\beta$ -Ta phase is formed during thin film growth whereas the bulk stable crystalline phase is the bcc  $\alpha$ -Ta one. Physical properties, such as mechanical properties or electrical conductivity, differ greatly between these two structural allotropes, so the presence of the  $\beta$ -phase may compromise thin film performance.

In the presented study, our approach is to understand the fundamental phenomena driving the nucleation and growth of the  $\beta$ -phase, with special emphasis on the stress generation during film growth. To this end, highly sensitive in-situ stress measurements by the substrate curvature technique (MOSS) were combined with resistivity measurements during growth, as well as ex-situ post deposition structural investigations (XRD, AFM, HRTEM). Growth of Ta films on neutral substrates (amorphous native oxide covered Si wafers) always results in the  $\beta$ -Ta phase, whereas a wide range of deposition energy conditions were explored. However, increased deposition temperature favours the  $\alpha$ -Ta phase, and the coexistence of both allotropes was investigated.

We address the issue of stress development and defect incorporation in these nanoscale layers. In the initial growth stages, surface stress evolution was shown to be consistent with a 2D growth of an amorphous Ta phase. This amorphous layer is retained until a critical thickness of  $\sim 2$  nm, without any significant stress development. At this critical thickness, the nucleation of  $\beta$ -Ta is observed, associated with a strongly compressive stress evolution which can be related to the incorporation of growth defects. During further growth, no phase transition towards the equilibrium  $\alpha$ -Ta is observed at room temperature. However,  $\alpha$ -Ta can be directly stabilized on a buffer layer (crystalline Mo), as epitaxial stress promotes the equilibrium phase.

The obtained experimental results are in good agreement with a nucleation and growth model taking into account the minimization of the surface/interface energy. In turn, this thermodynamic description explains the remarkable stability of the  $\beta$ -Ta phase in thin films at room temperature, and the need for higher deposition temperatures for stabilization of the  $\alpha$ -Ta phase.

ID-107

**Synthesis of diamond like phase from supersaturated solid solution of nickel-carbon system prepared by high energy milling***N. Kundan<sup>1</sup>, B. Parida<sup>1</sup>, A. Keshri<sup>2</sup>, P.R. Soni<sup>1</sup>**<sup>1</sup>Department of Metallurgical and Materials Engineering, Malaviya National Institute of Technology, Jaipur, India**<sup>2</sup>Department of Materials Science and Engineering, Indian Institute of Technology Patna, India*

Supersaturated solid solution having composition of Ni-15wt % C<sub>gr</sub> (graphite) was prepared by high energy ball milling of the elemental powders. The resultant powder was degassed and differential scanning calorimetry (DSC) was performed to determine the temperature for formation of diamond-like phase. The supersaturated solid solution was consolidated by hot pressing as well as by spark plasma sintering at 1000 °C under a pressure of 10 MPa. The high energy milled powder and the consolidated samples were characterized by XRD technique and Raman spectroscopy to confirm the formation of diamond-like phase. These studies have revealed the formation of diamond-like phase in the consolidated samples. It is believed that formation of diamond-like phase must have taken place during precipitation of the graphite in the nickel lattice during consolidation. Measurement of micro-hardness results shows that the yield of the diamond-like phase is more in the case of consolidation by hot pressing, which is due to prolonged precipitation duration. Aim of the present investigations was to develop a process for transformation of graphite into diamond at lower pressure and temperature as compared to HTPT process.

Keywords: High energy milling, Supersaturated solid solution, Hot pressing, Spark plasma sintering, Raman spectroscopy, Diamond-like phase.



Thursday 5 July morning - 11:30/13:00

Parallel Session 4  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES V**  
L. Gavioli

**ID-203 (invited)****New nanostructured composite materials with partially-carbonized elastomer matrix**

S. Kaloshkin

*National University of Science and Technology "MISIS"*

Development of new nanostructured polymer-based composite materials with high mechanical, thermal and other functional properties is an important area of materials science. At present, one of the main problems limiting the use of polymer composites is their low thermal stability. It is possible to improve the thermal stability of polymer matrix composite materials by complete or partial carbonization of the polymer matrix. As precursors of the carbonized matrix various synthetic rubbers and phenolic resins can be used. Nowadays the use of synthetic rubbers for this purpose does not found wide spreading, but it has undoubted practical interest. Elastomer matrixes allow to have high level of filling of composite with different kinds of agents, including the nanosized ones. New composite materials with working temperatures up to 400°C, obtained by partial carbonization of highly filled elastomeric compounds with carbon and ceramic fillers of various morphologies, are proposed. Low-temperature carbonization makes it possible to obtain thermally and dimensionally stable composite materials from elastomeric mixtures. Carbon composites exhibit rather high values of tensile and compression strength at relatively high impact toughness.

The paper presents data on the parameters of preparation and the properties of composite materials based on the carbonized elastomeric matrices in comparison with known polymer-based materials (PSU, PPS, PEEK). Materials with good mechanical properties, high heat-resistance and dimensional stability were obtained at the centre of composite materials of NITU MISIS jointly with companies "REAM-RTI" and "GRADER".

This work is supported by Ministry of Education and Science of Russian Federation (RFMEFI57815X0133).

## ID-95

**Consolidation of the  $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$  (wt%) atomized amorphous powder alloy by hot extrusion**

*R.D. Cava<sup>1</sup>, E.M. Mazzer<sup>2</sup>, C.S. Kiminami<sup>3</sup>, P. Gargarella<sup>3</sup>, C. Bolfarini<sup>3</sup>, W.J. Botta<sup>3</sup>, V.M. Pedrosa<sup>3</sup>*

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In the past two decades, metallic glasses (MGs) have drawn considerable attention due to their unique mechanical behavior and high corrosion resistance. Cu-based MGs are known for having excellent mechanical properties together with a high glass forming ability. These characteristics make these alloys important candidates for practical applications in structural areas such as “micro-engineering”, such as the fabrication of micrometric parts. Some quaternary Cu-based alloys, such as those belonging to the Cu-Zr-Al-(Nb, Y, Gd) and to the Cu-Zr-Hf-Al systems, presented a higher GFA. Cu-Zr-Al-Y system, have been shown unusual high GFA  $\text{Cu}_{46}\text{Zr}_{42}\text{Al}_7\text{Y}_5$  alloys have shown critical casting thickness up to 1 cm and a  $T_x$  of around 100 K. This alloy was used in this work to produce powders by gas atomization. Considering these aspects, large BMGs can be produced by consolidation from amorphous powders. The powder with granulometric range of 75 to 106  $\mu\text{m}$  were consolidated by hot extrusion in the super-cooled liquid region using an extrusion rate of 3:1 producing cylindrical amorphous bulks with  $\sim 8$  mm diameter and several mm long. The microstructural and thermal behaviors of the powders and the extruded amorphous bulk were characterized by X-ray, scanning (SEM) and transmission (TEM) electron microscopy and differential scanning calorimetric techniques. The results reported here contribute to open a new window in the manufacture and application of Copper based amorphous alloys indicating a successful processing route to obtain bulks in centimeter scale.

**ID-151****The influences of processing parameters on forming characterizations in the infrared heating type gas pressure forming system**

*K-R Lim, Y-H Kim, K-S Lee, Y-S Na*

*Korea Institute of Materials Science*

So far, various forming techniques toward amorphous materials have been developed. Gas pressurized molding is one of the useful forming techniques suitable for metallic glass sheet, since metallic glasses generally show good formability in the supercooled liquid region. It is advantageous on increasing the degree of precision, since there is little friction between the sample and the mold during the forming process. In addition, it enables the production of three-dimensional structure at a time. We adopted the infrared (IR) as a heating source to reduce process time and cost, since energy delivery of IR guide selectively heats the metallic glass sheet. To investigate the formability of the metallic glass sheet by this system, we prepared Zr-based metallic glass sheet with a width of 100 mm and a thickness of 100  $\mu\text{m}$  by melt spinning. In the present study, the effect of variables such as temperature, pressure and fragility on the formability will be discussed.

## ID-302

**Synthesis of manganese oxide nanoparticles for electrocatalysis applications using supercritical carbon dioxide**

*V. Zefirov, I. Elmanovich, E. Levin, S. Abramchuk, E. Kharitonova, A. Khokhlov, M. Kondratenko, M. Gal'yanov*

*Lomonosov Moscow State University*

Manganese oxides are known as promising electrocatalytic materials due to their significant activity and stability in alkaline media. The electrocatalytic activity of materials based on manganese oxides depends strongly on their morphology and particle size, which in turn are determined by the synthesis procedure. Usually, in methods for producing manganese oxides one uses an inorganic precursor, but an organic one can also be used to produce more dispersed and uniform materials. Usually to obtain disperse manganese oxides from an organic precursor one can either dissolve it in liquid solvent with subsequent thermal treatment, or use chemical vapor deposition method instead. However, both approaches have certain shortcomings. The main disadvantage of the former method is the possibility of undesirable reactions between the solvent and ligands during the stage of (thermo) destruction of the precursor. Moreover, it is required to induce the decomposition of the precursor only by applying high-temperature treatment as far as it is not desirable to introduce any additional destruction-initializing agents, since they may react with the solvent. As for the latter method, CVD allows one to obtain uniform thin films or agglomerated nanoparticles, yet the synthesis of non-agglomerated nanoparticles is a non-trivial task typically requiring some special approaches and equipment. One possible way to get rid of these drawbacks is switching to super-critical carbon dioxide (sc CO<sub>2</sub>) as an alternative solvent for electrocatalyst preparation. Sc CO<sub>2</sub> has high density like that of a liquid and can be used as a solvent for a number of organometallic precursors of manganese. At the same time, the absence of surface tension-driven effects makes its application promising for obtaining highly disperse materials with small grain size and high specific area. The main purpose of the present work is to demonstrate a novel method of preparing manganese oxide nanoparticles from organic precursor using supercritical CO<sub>2</sub>. In our approach, we dissolve metalorganic precursor in supercritical CO<sub>2</sub> and then thermally destroy organic phase in sc CO<sub>2</sub> media, saturated by O<sub>2</sub>, to produce oxide nanoparticles. As a result of the conducted experiments, highly dispersed manganese oxides mainly in the β-MnO<sub>2</sub> phase with high specific surface area and low polydispersity index were synthesized. In addition, reasonable electrocatalytic activity of the resulting material was found.

## ID-45

**Mechanical investigation approach to optimize the HVOF Fe-based amorphous coatings reinforced by B<sub>4</sub>C nanoparticles**

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*Department of Nanotechnology Engineering, Faculty of Advanced Sciences and Technologies, University of Isfahan*

Fe-based amorphous feedstock powders used as the matrix into which various ratios of hard B<sub>4</sub>C nanoparticles (0, 5, 10, 15, 20 vol%) as a reinforcing agent were prepared using a planetary high-energy mechanical milling. The ball-milled nanocomposite feedstock powders were also sprayed by means of high-velocity oxygen fuel (HVOF) technique. The characteristics of the powder particles and the prepared coating depending on their microstructures and Nanohardness were examined in detail using nanoindentation tester. The results showed that the formation of the Fe-based amorphous phase was noticed over the course of high-energy ball milling. It is interesting to note that the nanocomposite coating is divided into two regions, namely, a full amorphous phase region and homogeneous dispersion of B<sub>4</sub>C nanoparticles with a scale of 10–50 nm in a residual amorphous matrix. As the B<sub>4</sub>C content increases, the nanohardness of the composite coatings increases, but the fracture toughness begins to decrease at the B<sub>4</sub>C content higher than 20 vol%. The optimal mechanical properties are obtained with 15 vol% B<sub>4</sub>C due to the suitable content and uniform distribution of nanoparticles. Consequently, the changes in mechanical properties of the coatings were attributed to the changes in the brittle to ductile transition by adding B<sub>4</sub>C nanoparticles.

**KEYNOTE LECTURE**

G. Barucca

**Applications and potential of 3D printing: from polymers to magnetic solid state materials***D. Suess<sup>1</sup>, M. Groenefeld<sup>2</sup>, S. Schuschnigg<sup>3</sup>, M. Goertler<sup>4</sup>, C. Huber<sup>1</sup>**<sup>1</sup>Christian Doppler Laboratory for Advanced Magnetic Sensing and Materials, University of Vienna, 1090 Vienna, Austria**<sup>2</sup>Magnetfabrik Bonn GmbH, 53119 Bonn, Germany**<sup>3</sup>Department of Polymer Engineering and Science, Montanuniversitaet Leoben, 8700 Leoben, Austria**<sup>4</sup>Institute for Surface Technologies and Photonics, Joanneum Research Forschungsgesellschaft GmbH, 8712 Niklasdorf, Austria*

Within this talk I will give a review and status of 3d printing in various fields ranging from applications in gas turbines, to lenses for THz beam shaping [1] and magnetic materials [2]. A compilation of different additive manufacturing methods will be given with special focus on (i) fused deposition modeling (FDM) and (ii) selective laser melting (SLM) for additive manufacturing of magnets [2].

I will present that it is possible to produce NdFeB polymer bonded magnets with gradual change in magnetic properties, which is not possible to realize with any other method [3]. Furthermore, I will present first results on aligning anisotropic ferrite particles during printing that could allow in the future to realize magnets with locally varying magnetization directions such as Halbach arrays or undulators.

In order to fully make use of these new production flexibility advanced algorithm are required to determine the shape of the printed structure such as mechanical parts or magnets to meet the requirements for applications. I will introduce the efficient Adjoint Method as described in Ref [4] in order to solve the inverse field problem. As an example, I will present the fabrication of additive manufactured magnetic shimming elements to improve the homogeneity of a magnetic field. The simulation algorithm can find a suitable permanent and nonlinear soft magnetic design that fulfills the desired field properties.

I will conclude with an outlook how 3d printing may influence the design of functional materials and applications in the future.

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Thursday 5 July afternoon - 15:30/17:00

Parallel Session 1  
**MAGNETIC, TRANSPORT AND OPTICAL PROPERTIES FROM  
NANOSCALE TO BULK IV**  
P. Jonsson



**ID-248 (Invited)****Artificial all-amorphous magnetic superstructures**

*G. Muscas<sup>1</sup>, R. Brucas<sup>2</sup>; P. Jönsson<sup>1</sup>*

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<sup>2</sup> Uppsala University, Department of Engineering Sciences

Composites and superstructures represent one of the most effective ways to create new materials with improved properties. The rate of success of such approach depends on the degree of integration among the components of the composite and on the quality of the interfaces. Interfaces have a strong influence on magnetic properties but are difficult to control. We deal with the root of the interface problem through the use of a non-conventional approach, namely realizing fully amorphous system. By this choice, we can avoid the defects associated with crystalline interfaces. We have selected  $\text{Fe}_{89}\text{Zr}_{11}$  as a model amorphous material and we have modulated its magnetic properties by locally tuning the chemical composition by means of boron ion implantation through a mask, without inducing crystallization or any other major structural modification, obtaining amorphous  $\text{Fe}_{80}\text{Zr}_{10}\text{B}_{10}$  elements in regular patterns fully embedded in the original amorphous matrix. The investigation of a sample consisting of 20  $\mu\text{m}$  ferromagnetic discs embedded in a paramagnetic matrix by MOKE microscopy reveals a vortex as the ground state configuration, strongly suggesting an extremely low concentration of defects acting as pinning center for the magnetization reversal. When also the matrix is in a ferromagnetic state, the magnetic coupling between the two phases can extend over the micrometer-scale thanks to the structurally smooth transition between FeZrB and FeZr. This has been investigated by means of first-order reversal curves recorded with a longitudinal MOKE setup, which showed a single reversal of the two-phase sample. Our results open new perspectives for magnetic all-amorphous nano- and microstructures with tunable properties.

## ID-263

**Optimization of magnetic properties in (Hf,Cr)-Co-B alloys by structural transformations**

*A. Musiał<sup>1</sup>, Z. Śniadecki<sup>1</sup>, A. Klimametov<sup>2</sup>, J. Ivanisenko<sup>2</sup>, D. Wang<sup>2</sup>, J. Kováč<sup>3</sup>, B. Idzikowski<sup>1</sup>*

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Hard magnetic materials based on rare-earths elements are widely used due to their high energy product  $[BH]_{\max}$ . Investigation of new magnetic alloys is focused on compositions with reduced amounts of critical elements. Such systems should be characterized by at least half of the value of the energy product of Nd-Fe-B materials.

The Hf-Co-based alloys have high Curie temperature and magnetic anisotropy, but still are not sufficiently developed to fulfill all criteria to partially replace Nd-Fe-B materials. Grain refinement is believed to play a crucial role in further improvement of magnetic properties, especially anisotropy. It can be achieved by partial substitution or by thermomechanical treatment, as for example combined high pressure torsion (HPT) and isothermal annealing.

After isothermal annealing, magnetic measurement and x-ray diffraction of  $\text{Hf}_2\text{Co}_{11}\text{B}$  ribbons show coexistence of two  $\text{Hf}_2\text{Co}_{11}$  phases, crystallizing in different structures, with the rhombohedral one showing hard magnetic properties [1]. For this alloy the evolution of crystalline structure induced by heat treatment and high pressure torsion deformation and its influence on the magnetic properties of fully amorphous and partially crystalline  $\text{Hf}_2\text{Co}_{11}\text{B}$  ribbons were investigated. The amorphous material after annealing is characterized by coercive field of 0.7 kOe and after deformation this field is reduced to 0.2 kOe. Nonetheless, the subsequent reannealing of the deformed sample enhanced the coercivity up to 1.3 kOe. This shows that the combined HPT method and heat treatment allow tuning the structure and optimizing magnetic properties. The possibility of formation and properties of Cr substituted samples were also investigated.

Formation enthalpy of  $\text{Hf}_2\text{Co}_{11}\text{B}$  amorphous alloy  $\Delta H_{\text{am}} = -20.6$  kJ/mol, along with other thermo-dynamic parameters, indicate its moderate glass forming ability. For  $\text{Cr}_2\text{Co}_{11}\text{B}$  alloy  $\Delta H_{\text{am}} = -0.5$  kJ/mol, which suggests that its ability to form amorphous phase is rather low [2]. The results of semiempirical modelling are in good agreement with experimental results.

**Acknowledgments**

This work was supported by the National Science Centre, Poland, within the project No. 2016/23/N/ST3/03820.

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ID-331

## Correlation of magnetic and electrical properties of Co-rich amorphous ferromagnetic microwires after DC Joule heating treatment

*S. Gudoshnikov<sup>1</sup>; V. Odintsov<sup>2</sup>; B. Liubimov<sup>2</sup>; S. Menshov<sup>2</sup>; A. Popovs<sup>2</sup>; V. Tarasov<sup>1</sup>*

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In this work the electrical and magnetic properties of Co-rich amorphous glass-coated ferromagnetic microwires (AFM), having typical metallic core diameters  $d = 15 - 30 \mu\text{m}$ , were investigated under the DC Joule heating treatment. During DC Joule heating, a continuous monitoring of the AFM state was carried out by measuring its resistance using a DC bridge circuit. We used a program-controlled voltage source to power the bridge circuit, which allowed us to heat the AFM in various time modes and to monitor small resistivity variations. The heating process of the AFM sample, was performed at a linearly varying power at a speed of  $0.1 \text{ W/min}$  to a range values from  $0.8 \text{ W}$  to  $4.5 \text{ W}$ . The obtained dependence of the relative resistance allowed us to determine zones of the structural relaxation and the crystallization point of the AFM.

When the AFM was in crystallized state (power more  $2.8 \text{ W}$ ), its resistance dropped by 10% approximately as compared to initial state. The behavior of the AFM after additional heating of the treated crystallized samples was completely reversible and its plot is very close to the curve branch of cooling process. Variations of the AFM resistance correspond to relaxation transformations with the amorphous structure conservation, if the AFM was heated below crystallization threshold (power less  $2.8 \text{ W}$ ). The re-relaxation is accompanied with an increase of electrical AFM resistance. It was found that the growth of the AFM resistance, as a result of current heating, can reach  $\sim 1\%$  in comparison with its initial value. Relative increment of resistance depends on the values of the heating power and the heating time.

The studies of AFM magnetic properties were carried out using an induction method, the small angle magnetization rotation method and the giant magnetoimpedance technique. The saturation magnetization, the magnetostriction constant, the average value of the residual quenching stress and the giant magnetoimpedance ratio have been estimated. We found that the magnetic characteristics of the AFM correlate well with the value of the resistance measured during DC Joule heating process.

ID-349

**Structure formation and magnetic properties of alloys based on  $\text{Sm}_2\text{Fe}_{17}\text{N}_x$  compound after severe plastic deformation by torsion***I. Shchetinin<sup>1</sup>, V. Menushenkov<sup>1</sup>, R. Sundeev<sup>2</sup>, A. Menushenkov<sup>3</sup>, M. Platonov<sup>4</sup>, A. Rogalev<sup>4</sup>, A. Savchenko<sup>1</sup>*<sup>1</sup> National University of Science and Technology «MISIS»<sup>2</sup> Moscow Technological University, «MIREA»<sup>3</sup> National Research Nuclear University «MEPhI»<sup>4</sup> European Synchrotron Radiation Facility (ESRF)

The nitrides of the  $\text{Sm}_2\text{Fe}_{17}$ -based alloys are promising for development of permanent magnets since they have a high magnetic anisotropy constant, Curie temperature, and contain less rare-earth metals compare to  $\text{Nd}_2\text{Fe}_{14}\text{B}$  compound. In this connection the study of the regularities in the formation of the structure and magnetic properties of the  $\text{Sm}_2\text{Fe}_{17}$  nitrides after severe plastic deformation is an urgent task both from a scientific and practical point of view.

Structure formation and magnetic properties of alloys based on  $\text{Sm}_2\text{Fe}_{17}\text{N}_{2,8}$  compound after severe plastic deformation by torsion has been studied. The nitrides of  $\text{Sm}_2\text{Fe}_{17}$  compound were obtained by multiple hydrogenation-dehydrogenation and followed nitrogenation at 450 ° C for 40 hours. The severe plastic deformation was performed in the Bridgman camera with pressure 6 GPa. X-ray diffraction analysis was carried out on a Rigaku Ultima IV diffractometer using  $\text{CoK}\alpha$  radiation. Spectrum analysis was carried out using the software PDXL (Rigaku). The microstructure of the alloys was studied at electron microscope TESCAN VEGA 3 SBH. Measurement of magnetic properties was carried out using a PPMS (Quantum Design). The XMCD studies have been performed at the European Synchrotron Radiation Facility (ESRF) at ID12 station in fields up to 170 kOe.

The alloys in initial state and after hydrogenation and dehydrogenation processes contained main phase of  $\text{Sm}_2\text{Fe}_{17}$  and a small amount (<2%) of  $\alpha$ -Fe. Nitrogenation resulted to increase lattice spacing of  $\text{Sm}_2\text{Fe}_{17}$  phase without formation of new phases. After severe plastic deformation diffraction patterns have a strong broadening of diffracted lines which indicated formation of fine structure and confirmed by SEM data: formation of equiaxial structure with average grain size about 20 nm. According to X-ray diffraction analysis the fraction of  $\alpha$ -Fe increased during severe plastic deformation process due to local heating of sample and decomposition of the  $\text{Sm}_2\text{Fe}_{17}\text{N}_{2,8}$  phase. The hysteretic properties of alloys changed non-monotonic: after deformation of  $n = 2.5$  coercive force was increased to 6.5 kOe but further increase of deformation degree led to a decrease in coercive force. The XMCD data confirm decomposition  $\text{Sm}_2\text{Fe}_{17}\text{N}_{2,8}$  phase during severe plastic deformation.

The work was supported by the Ministry of Science and Education of the Russian Federation under the of the Russian Federation President grants for state support of young Russian scientists, grant No. MK-3616.2017.2.

ID-377

**Giant magnetoimpedance effect in  $\text{Co}_{66.5}\text{Fe}_{3.5}\text{Si}_{12.0}\text{B}_{18.0}$  amorphous ribbons layered with Co film**

V Vega<sup>1</sup>, V.M. Prida<sup>1</sup>, L Domínguez<sup>2</sup>, P Corte-León<sup>3</sup>, M Ipatov<sup>4</sup>, A Chizhik<sup>3</sup>, V Zhukova<sup>3</sup>, A Zhukov<sup>3</sup>, B Hernando<sup>1</sup>, J González<sup>3</sup>

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<sup>4</sup> University of the Basque Country

This work reports on Giant magnetoimpedance effect (GMI) of nearly-zero magnetostrictive  $\text{Co}_{66.5}\text{Fe}_{3.5}\text{Si}_{12.0}\text{B}_{18.0}$  amorphous ribbons in as-cast state and covered by a Co layer has been investigated in the frequency range of 10 MHz – 1.5 GHz. Ribbons were fabricated by the melt-spinning technique using a Fe wheel in a 10-3 mbar vacuum chamber and with 0.60 mm of width, and around 23  $\mu\text{m}$  thick. A uniform Co layer was deposited on the surface of some pieces of the amorphous ribbon by electrochemical de-position. The microstructure and composition of as-cast and cobalt coated samples were studied by Scanning Electron Microscopy (SEM JEOL-6610LV) equipped with Energy Dispersive X-ray analysis (EDX). Hysteresis loops have been performed at 300 K, by a Vibrating Sample Magnetometer (VSM, VersaLab, QD), at applied magnetic fields up to  $2.4 \times 10^3$  kA/m for both samples. The impedance of 1 cm long samples was measured with a N5230A vector network analyzer at moderate frequencies 10-100 MHz and at high frequencies 1.0-3.5 GHz [1]. Comparison among GMI responses of these ribbons with and without Co layer is discussed. It is remarkable that a more defined structure with respect to the two peaks-behavior of GMI effect is observed in the ribbon with Co layer, although the intensity of the peaks is larger in the as-cast ribbon.

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Thursday 5 July afternoon - 15:30/17:00

Parallel Session 2  
**NANOSTRUCTURED MATERIALS XI**  
T. Sarkar

**ID-280 (Invited)****Nanogranular materials obtained by gas phase synthesis: physical properties and multimodal multiscale metrology**

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Nanogranular materials are composed by nanoparticles (NP) assembled in 3D arrangements, in which the single NP is keeping its identity but is surrounded by similar blocks. The peculiar physical properties, applicable in energy [1,2] microbiology [3-5] medicine [6] and nanotechnology [7], results from the single NP composition and the NP arrangement. The nature of such systems is in fact spanning from the nano to the micro scale. Hence a multimodal and multiscale approach is needed to understand and engineering the behavior of granular materials.

In this talk, we synthesize granular materials by a flexible route, i.e. the supersonic cluster beam deposition (SCBD), based on gas phase synthesis of NP aggregated into a supersonic beam. The beam is employed to deposit a granular film with nominal thicknesses ranging from less than one layer up to hundred nm. The NP are composed of single or multielements, e.g. Ag, AgTi, AgCuMn.

On the nanoscale, the morphology and composition are inspected via Atomic Force Microscopy, X-Ray Diffraction, transmission electron microscopy (TEM) and Photoelectron Spectroscopies. On the mesoscale a virtual film model is proposed merging TEM, supersonic cluster beam dynamics and molecular dynamics simulations. The model is validated against microscale mechanical nanometrology measurements [8,9] and spectroscopic ellipsometry [10]. The model, readily extendable to metals other than Ag, is shown to be a flexible and reliable predictive tool to access morphology-dependent properties such as mesoscale gas-dynamics and elasticity.

The results show that it is possible to: 1) tailor the NP properties (size, purity, crystallinity); 2) obtaining the granular film directly on surfaces (type of surface, NP density); 3) predict and engineer the granular material properties (adhesion, mechanical behavior).

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## ID-77

**Preparation and characterization of Pt/C nanotubular heterostructures by a simple vapor deposition method**

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Nanotubular heterostructures have many desirable properties, which can be modulated by fitting their composition, morphology and size. In this work, we report the preparation of Pt/C nanotubular heterostructures by a novel simple vapor decomposition method consisting in two-steps procedure. In an initial step, a mixture of f-CNTs and Pt precursor (Pt-acac) was heated in a quartz reactor at 180 for 10 min at 5, 50 and 560 torr. In a second step, the temperature was increased at 450 °C for 5, 10 and 20 min in flowing Ar (100 cm<sup>3</sup>/min). The functionalization of CNTs (f-CNTs) was achieved with HNO<sub>3</sub> (60% v/v) to generated oxygen functional groups. The presence of functional groups was verified by FT-IR. Pt incorporation was favored as a consequence of the functionalization treatment. These results suggest that functional groups served as nucleation sites for Pt phase on the surface of CNTs. X-ray diffraction, SEM and TEM results reveled that pressure has a significant effect on the morphology of Pt. Whereas highly dispersed Pt nanocrystals of about 5 nm in size were deposited at 5 torr, larger Pt crystals of about 20 nm, forming a quasi-continuous phase, were obtained on the surface of Pt CNTs at 560 torr. Pt nanocrystal size was controlled as a function of the working pressure. Pt/C nanotubular structures exhibit a middle absorption about 40% in the range of 210 to 350 nm<sup>-1</sup> having potential applications in the development of optoelectronic devices.



## ID-172

**Using phenol formaldehyde resin and organic compound vapors to synthesize graphite encapsulated nickel nanoparticles in an arc-discharge system***Y-C Huang, M-H Teng**National Taiwan University*

Graphite encapsulated nickel nanoparticles (Ni-GEM) are a kind of core-shell magnetic composite nanomaterial with an average particle size between 5 to 100 nm. Because of the protection of the outer turbostratic graphite shell, the nanocrystalline metal core can be preserved in a severe environment, i.e. acid erosion or oxidation, providing a great application potential for environmental and biomedical engineering. An arc-discharge synthesis process of the Ni-GEM has recently been modified by using alcohols as the carbon source, and this has improved both the encapsulation efficiency and production yield up to 80% and 14 g/h, respectively. However, the injection of alcohols destabilized the arc-discharge due to the dramatic changes in the electrical resistance caused by the decomposition of the alcohol and may even have led to the disruption of the whole experiment. In this study, instead of using the alcohol injection method, we use colloidal phenol formaldehyde resin (PF resin) as the carbon source. The PF resin will gradually graphitize and release both hydrogen and carbon ring molecules at temperatures above 300 . The newly formed graphite can then be evaporated along with nickel to form Ni-GEM. Moreover, a volatile organic compound, i.e. benzene or cyclohexane, is placed next to the anode providing additional carbon vapor near the arc-discharge area. The new experimental setup effectively provides enough carbon vapors, avoids electrical resistance changes, and maintains the stability of the arc. Preliminary results show that the production yield can be greatly increased to 30 g/h, and the encapsulation efficiency is maintained at ~80%. This work demonstrates a new method for mass production of Ni-GEM nanoparticles and reveals a different encapsulation mechanism from the conventional one.

**ID-150****Nano-structured CoCrFeMnNi high-entropy alloy produced by cryogenic multi-pass caliber rolling**

*J-W Won, K-R Lim, Y-S Na*

The ultrafine-grain (UFG) structure of CoCrFeMnNi high-entropy alloy was achieved using cryogenic multi-pass caliber rolling imposing a relatively low deformation of  $e = 1$  compared to severe plastic deformation (SPD,  $e > 4$ ). Highly enhanced twinning activity at 77 K together with operation of multi-variant twins caused the grain interiors to very effectively fragment, making it possible to induce UFG structure ( $\sim 100$  nm) without imposing SPD. The processed material showed an exceptional high yield strength of  $\sim 1.5$  GPa with a reasonable elongation of  $\sim 10\%$  at room temperature.

Thursday 5 July afternoon - 15:30/17:00

Parallel Session 3  
**MECHANICAL PROPERTIES II**  
D. Barreca

**ID-216 (Invited)****Comparing structural and mechanical properties of additive manufactured metallic parts after selected thermal treatments**

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Powder bed fusion (PBF) is an Additive Manufacturing (AM) process in which a metal powder is laid in a bed and sintered or melted by means of a high-energy beam, often a laser. Nowadays, PBF is penetrating specific markets by opening new technological opportunities for high-end products because of unique features such as: ground-breaking freedom of design allowing for extremely lightweight components with novel and integrated functionalities, fast production times, high flexibility, and reduced costs. In their practical use, PBF components are often subjected to thermal stresses, such as the firing cycle typical of dental applications, used to fix ceramic to the metallic prosthesis, or the high temperatures reached by engine components in the automotive field. In this work we present a structural and mechanical investigation of components produced by laser PBF starting from powders of three different alloys: CoCr, Ti<sub>6</sub>Al<sub>4</sub>V and AlSiMg. The effect of selected thermal treatments on the as-sintered parts has been investigated using X-ray diffraction, electron microscopy techniques and mechanical tests. The cobalt alloy is typically used for biomedical applications and results showed the microstructure of the as-sintered sample composed of an intricate network of thin  $\epsilon$ -Co lamellae distributed inside the  $\gamma$ -Co phase matrix. The firing cycle leaves this structure unchanged although a massive presence of coarse precipitates is observed, together with a slight modification of the mechanical properties. Ti6Al4V is widely used for dental applications. The microstructure of the as-sintered samples, due to the PBF rapid cooling, is acicular martensitic  $\alpha'$  titanium phase. The firing cycle induces the  $\beta$  phase formation at the  $\alpha$  plate boundaries leading to reduced values of strength, with respect to the as-sintered samples. AlSiMg sintered parts have mechanical properties suitable for automotive applications, but thermal treatments simulating their implementation in engines, showed the extensive formation of pores resulting in a dramatic reduction of the mechanical properties. Understanding the effect of thermal treatments on the structure and mechanical properties of PBF sintered objects is of paramount importance for their practical applications.

ID-397

**Mechanical properties of a hot rolled and annealed medium Mn automotive steel**

*J.L. Hernandez Rivera<sup>1</sup>, E. Palma-Elvira<sup>2</sup>, S. Pacheco-Cedeño<sup>3</sup>, J. Cruz-Rivera<sup>2</sup>, J. Garcia-Rocha<sup>2</sup>, C. Garay-Reyes<sup>4</sup>*

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This research is focused in the development of a medium Mn steel for potential automotive use. Ferrosilicon, Aluminum and electrolytic Mn were added to 1018 steel scrap in an induction furnace in order to obtain this steel. The composition was measured by optical emission spectroscopy and it was 9wt% of Mn, 1.5 wt% of Si, 1.4 wt% of Al and 0.14wt% of C. Ingots were hot rolled at 1100°C by approximately 12 passes in order to reduce the thickness from 40 to 2.5 mm. The microstructural characterization was made by optical and scanning electron microscope and it was found the presence of austenite, ferrite and two types of martensite: cubic  $\alpha'$  and hexagonal  $\epsilon$ . It was observed that there was a significant reduction in hardness from the as-cast material to the hot rolled product. An inter-critical annealing heat treatment was designed in order to obtain a mix of ferrite and austenite at room temperature. The presence of austenite at room temperature was verified by X-ray diffraction. There was an important increment in the tensile properties after the annealing treatment that was attributed to the deformation and transformation of austenite during straining.

## ID-213

**A heat treatable TiB<sub>2</sub>/Al<sub>3.5</sub>Cu<sub>1.5</sub>Mg<sub>1</sub>Si composite fabricated by selective laser melting**

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Selective laser melting (SLM) is one of the emerging layer-wise additive manufacturing techniques that allows generating complex 3D parts. Because of the high degree of freedom in the shape and geometry of the SLM parts, along with the non-equilibrium phases and fine microstructures resulting from rapid solidification during SLM processing, a progressively expanding spectrum of composites has been processed by SLM. The present work compares the microstructure and mechanical properties of a heat treatable TiB<sub>2</sub>/Al<sub>3.5</sub>Cu<sub>1.5</sub>Mg<sub>1</sub>Si composite synthesized by SLM with the un-reinforced Al-Cu-Mg-Si alloy. The results reveal that the addition of the TiB<sub>2</sub> particles results in a remarkable grain refinement, leading to enhanced strength of the TiB<sub>2</sub>/Al-Cu-Mg-Si composite. After heat treatment, the grain refinement and precipitation hardening contribute to the high compressive strength of the TiB<sub>2</sub>/Al-Cu-Mg-Si composite.

Thursday 5 July afternoon - 15:30/17:00

Parallel Session 4  
**APPLICATIONS I**  
S. Enzo

**ID-378 (Invited)****High strength Ti-based alloys for structural and biological applications***D. Louzguine-Luzgin**WPI Advanced Institute for Materials Research, Tohoku University*

Ti-Fe-Sn-Nb hypoeutectic dual-phase alloys consisting of primary dendritic  $\beta$ -Ti crystals and ultrafine  $\beta$ -Ti+TiFe eutectic possess superior mechanical properties [1]. For example, the as-cast  $\text{Ti}_{67}\text{Fe}_{27}\text{Sn}_3\text{Nb}_3$  (at. %) alloy exhibits exceptionally high yield stress of 2.18 GPa, significant strain-hardening on deformation and good plasticity of 12 %. The slip deformation and accumulation of dis-locations in the  $\beta$ -Ti dendrites contribute to the plasticity and pronounced strain-hardening, whereas the high strength stems from the ultrafine eutectic structure as well as the solution hardening induced by Fe as one of the most effective strengthening elements for  $\beta$ -Ti.  $\beta$ -Ti solid-solution type  $\text{Ti}_{80}\text{Fe}_{14}\text{Sn}_3\text{Nb}_3$  alloy also exhibited a high yield stress of 1.88 GPa along with the plastic deformation of 32 % [2]. Such a high strength is about 50 % higher than the values typical for conventional  $\beta$ -Ti alloys and comparable to those of Ti-based nanocrystalline alloys. The excellent mechanical strength is attributed to high stability of the supersaturated  $\beta$ -Ti and high den-sity of lattice defects that restrict the dislocation motion. A high strength Ti-Zr-Pd-Cu-Sn-Nb bulk glassy alloy showed a high corrosion resistance and low current density of approximately in 1 mass% lactic acid, phosphate-buffered saline solution and Hank's balance salt solution lower than that for pure Ti and Ti-6Al-4V alloy [3].

-Ti and + -Ti type Ti-Fe-Cu, Ti-Pd-Au and Ti-Pd-Nb alloys were found to have relatively good mechanical properties and a high capability to improve these properties by the dual-axial forging treatment [4,5]. Their elastic modulus of about 80-90 MPa is attractive for biological applications. These alloys also exhibited good corrosion resistance and a similar or even higher level of cell proliferation compared to the classical Ti-Al-V alloy.

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[2] G.-H. Zhao, S.V. Ketov, J. Jiang, H. Mao, A. Borgenstam, D.V. Louzguine-Luzgin, *Materials Science and Engineering: A*, 705, 348-351 (2017).

[3] J.-J. Oak, D. V. Louzguine-Luzgin, A. Inoue, *Materials Science and Engineering C* 29, 322-327 (2009).

[4] V.Yu. Zadorozhnyy, X. Shi, D.S. Kozak, T. Wada, J.Q. Wang, H. Kato, D.V. Louzguine-Luzgin, *Journal of Alloys and Compounds*, 707, 291-297 (2017).

[5] V.Yu. Zadorozhnyy, D.S. Kozak, X. Shi, T. Wada, D.V. Louzguine-Luzgin, H. Kato, *Journal of Alloys and Compounds*, 732, 915-921 (201)



ID-285

**Tunable corrosion behavior of calcium phosphate coated Fe-Mn-Si alloys for bone implant applications***R. Drevet, Y. Zhukova, P. Kadirov, S. Dubinskiy, A. Kazakbiev, Y. Pustov, S. Prokoshkin**National University of Science and Technology "MISIS"*

The Fe-Mn-Si alloys are promising materials as biodegradable metallic implants for temporary healing processes inside the human body. Their appropriate degradation properties in a physiological environment are used to avoid repeated surgical intervention for the implant removal after the completion of the healing process [1]. Moreover, the Fe-Mn-Si alloys are promising bone implant materials thanks to their appropriate biomechanical compatibility and mechanical reliability with the bone tissues [2].

In this work, the corrosion behavior of Fe-Mn-Si alloys is explored for three different alloy compositions ( $\text{Fe}_{23}\text{Mn}_5\text{Si}$ ,  $\text{Fe}_{26}\text{Mn}_5\text{Si}$  and  $\text{Fe}_{30}\text{Mn}_5\text{Si}$ , all in wt.%). Moreover, the influence of electrodeposited calcium phosphate coatings on the corrosion behavior of the Fe-Mn-Si alloys is studied. The electrodeposition process is carried out from two different electrolyte solutions, one with no  $\text{H}_2\text{O}_2$  and the other one with 9 vol.%  $\text{H}_2\text{O}_2$ . The physicochemical characterizations show that the electrodeposited coating is made of an apatite phase of low crystallinity with less porosity when hydrogen peroxide is added to the electrolyte solution. The corrosion measurements of the uncoated and coated alloys are assessed during immersions in Hank's solution at 37 °C, a physiological solution that simulates the inorganic composition of the body fluids. The results show that the manganese amount in the alloy and the porosity of the coating both modify the corrosion properties, i.e. the biodegradability of the alloy in the physiological environment. Therefore, the corrosion behavior of the calcium phosphate coated Fe-Mn-Si alloys can be tuned as a function of the experimental conditions used during the synthesis of the material.

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[2] R. Drevet, Y. Zhukova, P. Malikova, S. Dubinskiy, A. Korotitskiy, Y. Pustov, S. Prokoshkin, *Metal-lurgical and Materials Transactions A* 49,1006-1013 (2018).

ID-497

**Biodetection of histamine in wine: magnetic versus plasmonic labels**

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Histamine is a biogenic amine present in different kind of foods where a fermentation process is carried out by certain bacteria and yeasts. Due to this fact, fish, meat, cheese, vegetables, chocolate, beer or wine may have a certain amount of histamine. Besides, it increases with maturation time. 1% of the population is intolerant to histamine, but even in healthy individuals a high amount of histamine could cause increased gastric acid secretion and heart rate, headache, urticaria, pruritus and tachycardia, bronchospasm or cardiac arrest [1].

The determination of histamine is usually done following complex and time-consuming methods, such as chromatography, enzymatic and ELISA tests [2]. However, the control of histamine on-site during the fermentation processes would be an interesting option for food industries, in order to manage the quality of their products. In this work, a rapid, cheap and simple test for the detection and quantification of histamine in wine is presented. A competitive lateral flow immunoassay (CLFI) has been designed by using two types of different labels: magnetic (iron oxide) or plasmonic (gold) nanoparticles. In the former case, the quantification of the test relies on the superparamagnetism of the particles measured by a high frequency magnetic sensor [3,4], while in the latter it is done by reflectance measurements using a commercial optical strip reader. CLFIs are the preferred format to detect small molecules in lateral flow immunoassays. In these, a synthetic complex of the antigen–protein to be detected is immobilized on the nitrocellulose membrane of the strip forming the test line. These latter will compete with histamine present in the sample for the binding sites of the anti-histamine antibody which is added to the sample. When flowing by capillarity, only the free antibodies will get trapped by the histamine immobilized on the test line. Afterwards and as a developing step, a solution with one of the two labels conjugated with protein G is run through the strip. This protein has a high affinity for the Fc chains of the antibodies and gets therefore trapped at the test line. Its signal will be either magnetic or coloured but its intensity is for both inversely proportional to the concentration of histamine in the sample.

This methodology was followed to analyse histamine in wine samples, with a range concentration from  $10^{-6}$  to  $10^{-1}$  mg/mL for both types of labels. The conclusion is that, although gold nanoparticles are easier to functionalise, the magnetic test enables a better quantification which is absolutely independent of the tint that the wine (mainly red or rose wine) give to the membrane strip.

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- [2] Önal, A. Food Chemistry. 103, 1475 – 1486 (2007)
- [3] Lago-Cachón, D. et al. Nanotechnology, 24 (2013)
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ID-436

**Study of the structure and functional properties of metastable beta Ti<sub>18</sub>Zr<sub>14</sub>Nb (at.%) alloy for biomedical applications subjected to combined thermomechanical treatment***V. Sheremetyev<sup>1</sup>, A. Kudryashova<sup>1</sup>, S. Galkin<sup>1</sup>, S. Prokoshkin<sup>1</sup>, V. Brailovski<sup>2</sup>*<sup>1</sup> National University of Science and Technology "MISIS"<sup>2</sup> Ecole de Technologie Supérieure

The metastable Ti-Zr-Nb shape memory alloys (SMA) are considered as a promising material for load-bearing biomedical applications due to their unique combination of high strength, low elastic modulus, super-elastic behavior mimicking mechanical behavior of bone tissues, good deformability, superior corrosion resistance, and only non-toxic components [1]. The functional properties of Ti-Zr-Nb SMA can be effectively improved by thermomechanical treatment (TMT) [2]. Obtaining of a desired semi-product for bone implant fabrication and forming of a specific material microstructure to provide the best combination of functional properties could be realized by application of a combination of various metal forming techniques with heat treatment. It was shown, that application to Ti-18Zr-14Nb SMA of the novel combination of radial shear rolling (RSR) with thermomechanical treatment including longitudinal cold rolling and post-deformation annealing at different temperatures with the objective of forming various structures in long-length bars dedicated for bone implants fabrication successfully increases the combination of functional properties [3].

In this work, Ti<sub>18</sub>Zr<sub>14</sub>Nb (at.%) alloy was subjected to a hot deformation at 900 by RSR followed by rotary forging at 600 and 800, cold rotary forging with a true strain of  $\epsilon=0.3$ , and post-deformation annealing (PDA) in the 450-750 range for 0.5 h. Thus, the long-length bars were obtained for the following investigation of structure and functional properties. Structure studies were carried out by optical microscopy, X-ray diffractometry, and transmission electron microscopy. The mechanical properties were determined using tensile testing. The functional behavior was studied using the constant-strain temperature scanning and functional fatigue testing techniques. It is shown, that combination of RSR and rotary forging with PDA processing steps constitutes a promising approach to manufacture long-length bars with specific material microstructure and high complex of functional properties.

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2. S. Prokoshkin, V. Brailovski, S. Dubinskiy, Y. Zhukova, V. Sheremetyev, A. Konopatsky, K. Inaekyan. Shape Memory and Superelasticity 2(2), 130-144 (2016).
3. V. Sheremetyev, A. Kudryashova, S. Dubinskiy, S. Galkin, S. Prokoshkin, V. Brailovski Journal of Alloys and Compounds 737, 397-425 (2018).

ID-465

**Structural Investigation of modified bitumens by physical chemistry techniques***C.O. Rossi<sup>1</sup>, P. Calanra<sup>2</sup>, M.P. De Santo<sup>3</sup>, B. Teltayev<sup>4</sup>, R. Angelico<sup>5</sup>*<sup>1</sup> *Department of Chemistry and Chemical Technologies, University of Calabria*<sup>2</sup> *CNR-ISMN, National Council of Research*<sup>3</sup> *Department of Physics and CNR-Nanotec, University of Calabria*<sup>4</sup> *Kazakhstan Highway Research Institute*<sup>5</sup> *Department of Agricultural, Environmental and Food Sciences (DIAAA), University of Molise*

Bituminous binders are organic materials whose binding and hardening properties are caused by the temperature-related change of adhesion and cohesion of their molecules. Bitumen is often characterized by its chromatographic fractions, the maltenes (saturates, aromatics and resins) and the asphaltenes, soluble and insoluble in n-heptane respectively. The structure of bitumen is commonly modeled as a colloid, with maltenes as the continuous phase and micelles of asphaltenes stabilized by associated resins as the dispersed phase [1]. Here the composition and the colloidal structure is described by its physical and rheological properties.

In this work, we want to explore, by different physical chemistry techniques as AFM, Time-Domain Nuclear Magnetic Resonance (TD-NMR), Rheology and Wide Angle X ray Scattering (WAXS), the influence of some opportunely chosen surfactants on the bitumen structure with the aim to ultimately correlate the structural findings with the bitumen performances.

Thursday 5 July afternoon - 17:30/18:30

Poster session 4  
**ADVANCED PREPARATION AND PROCESSING TECHNIQUES**  
T. Sarkar

ID-49

**Investigations of V content, mechanical alloying and sintering on characteristics of tungsten-vanadium-yttria alloys***C.-L. Chen, S.-H. Ma**Department of Materials Science and Engineering, National Dong Hwa University, Hualien 97401, Taiwan*

Tungsten-based ODS alloys are considered as promising materials for the future fusion devices, in particular for the divertor and other first wall components. In this study, W-V-Y<sub>2</sub>O<sub>3</sub> alloys with varied V contents between 1 wt.% and 7 wt.% fabricated by mechanical alloying were investigated. The results suggest that vanadium concentration can significantly change microstructural homogeneity and distribution of fine oxide particles. In addition, high-energy ball milling can facilitate a solid-state reaction between the dispersed Y<sub>2</sub>O<sub>3</sub> particles and the tungsten-vanadium matrix and the subsequent sintering processing promotes the formation of complex V-rich oxide particles, which greatly increase the mechanical properties of the alloys. The different sintering methods were also discussed in this study.

ID-59

**Microstructural aspects of ultra-high-strength FeCrMoV(W)C alloys fabricated by selective laser melting***U. Kuehn, Jan Sander, J. Hufenbach, L. Giebeler, T. Gemming**Leibniz-IFW Dresden*

Selective laser melting (SLM) is an additive manufacturing process which enables high cooling rates leading to highly refined microstructures and to the formation of non-equilibrium phases of the alloy. This study investigates the influence of the SLM process on FeCrMoV(W)C alloys regarding microstructure and mechanical behavior. The presented microstructures are composed of a nanoscale carbide network, retained austenite and martensite. Caused by the fast directional cooling, a completely dendritic solidification aligned in building direction takes place. Non-equilibrium segregation leads to an orderly phase sequence of: carbide network at the boundary of the dendrites, surrounded by retained austenite, and martensite in the center of the dendrites. Furthermore, a strong work-hardening behavior is observed, based on an austenite-to-martensite phase transformation (TRIP effect). This leads to outstanding mechanical properties like a compression strength up to 6000 MPa.

In conclusion, the findings reveal that SLM is advantageous for the processing of ultra-high-strength FeCrMoV(W)C tool steels.



ID-186

**XRD, TEM and DTA studies of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  compound formed by mechanochemical and heat treatment processes***D. Oleszak<sup>1</sup>, M. Krasnowski<sup>1</sup>, T. Pikula<sup>2</sup>, M. Pawlyta<sup>3</sup>, M. Senna<sup>4</sup>, H. Suzuki<sup>5</sup>*<sup>1</sup> Faculty of Materials Science and Engineering, Warsaw University of Technology<sup>2</sup> Electrical Engineering and Computer Science Faculty, Lublin University of Technology<sup>3</sup> Institute of Engineering Materials and Biomaterials, Silesian University of Technology<sup>4</sup> Faculty of Science and Technology, Keio University<sup>5</sup> Research Institute of Electronics, Shizuoka University

Garnet type cubic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (c-LLZO) is regarded as a promising material for solid state electrolyte for Li-ion batteries. The basic idea is to synthesize this compound applying mechanochemical processes followed by appropriate heat treatment. This work describes the influence of mechanochemical processes parameters and subsequent heat treatment on the single-phase c-LLZO synthesis, starting from the powder mixtures consisting of highly reactive precursors of  $\text{ZrO}_2$ ,  $\text{La}(\text{OH})_3$  and  $\text{Li}_2\text{CO}_3$ . The XRD, TEM and DTA experimental techniques were employed for the studies and powders characterization.

ID-193

## Plasma-assisted synthesis and characterization of $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ -Au nanomaterials for light-activated functional applications

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Over the last decade, an increasing attention has been devoted to photo-activated processes for sustainable energy generation and purification/cleaning processes [1]. In this context  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$  nanocomposite systems, eventually functionalized with Au nanoparticles, have emerged as attractive candidates for the possibility to synergistically benefit from the single component feature, ultimately leading to an improved radiation harvesting and a reduced charge carrier recombination [2]. The attainment of such goals is of crucial importance for eventual end uses of the target nanomaterials in photo-assisted applications, encompassing both pollutant degradation and energy generation. The functional properties of  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ -Au systems are directly dependent on the intimate contact between the constituents and on a detailed morphology control, which, in turn, can be tailored by a proper choice of the preparation route. To this regard, the present work proposes a plasma-assisted approach for the fabrication of  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ -Au nanosystems with tunable chemical-physical properties, based on: i) the plasma-enhanced chemical vapor deposition (PE-CVD) of  $\text{Fe}_2\text{O}_3$  nanosystems on fluorine-doped tin oxide (FTO) substrates; ii) the sequential radio frequency (RF)-sputtering of titanium and gold; iii) thermal treatments in air. The adopted procedure yielded high purity nanocomposites characterized by the presence of alpha- $\text{Fe}_2\text{O}_3$  (hematite), the most thermodynamically stable polymorph of iron(III) oxide, an amorphous ultra-thin  $\text{TiO}_2$  over-layer, and Au gold nanoparticles with controlled spatial distribution. A thorough characterization of the obtained systems was carried out by complementary analytical techniques, with particular regard to their structure, chemical composition [3], morphology and optical properties. Finally, materials were preliminarily investigated in photoelectrochemical water splitting and self-cleaning applications, whose results highlighted the critical importance of controlling  $\text{Fe}_2\text{O}_3$ - $\text{TiO}_2$ -Au interfacial interactions in order to develop multi-functional nanocomposite systems for light-assisted processes.

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[2] D. Barreca et al., *Journal of Advanced Microscopy Research* 10, 239 (2015)

[3] D. Barreca et al., *Surface Science Spectra* 23, 61 (2016)

ID-210

**Experimental and theoretical study of two Mn (II) molecular precursors for chemical vapor deposition of Mn<sub>3</sub>O<sub>4</sub> nanomaterials**

*L. Bigiani*<sup>1</sup>, *C. Maccato*<sup>1</sup>, *G. Carraro*<sup>1</sup>, *A. Gasparotto*<sup>1</sup>, *R. Seraglia*<sup>2</sup>, *A. Devi*<sup>3</sup>, *G. Tabacchi*<sup>4</sup>, *E. Fois*<sup>4</sup>, *D. Barreca*<sup>2</sup>

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The development of Mn<sub>3</sub>O<sub>4</sub>-based functional systems, ranging from photocatalyst to gas sensors [1], has received a great attention thanks to their stability, environmental compatibility and low cost. In this scenario, the synthesis of Mn<sub>3</sub>O<sub>4</sub> nanosystems endowed with tailored structure, morphology, and composition is of crucial importance in view of the target end-uses [1]. To this regard, chemical vapor deposition (CVD) represents an appealing synthetic method for the preparation of multifunctional nanomaterials which allows a fine tuning of the resulting material properties, as a function of the adopted synthetic parameters. The potential of CVD is strongly dependent from the availability of adequate molecular precursors characterized by three main fundamental characteristics: high stability, volatility and clean fragmentation pathways.

In this work, we focus our attention on the synthesis of two Mn(II) complexes of formula Mn(hfa)2TMEDA (hfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate; TMEDA=N,N,N',N'-tetramethylethylenediamine) and Mn(tfa)2TMEDA (tfa = 1,1,1-trifluoro-2,4-pentanedionate) and their subsequent use as molecular precursors in CVD experiments. In order to thoroughly analyze the chemico-physical properties of the two target molecules, we adopted a synergic experimental-theoretical approach which allows us to confirm their high stability to air/moisture, single-step vaporization, and clean fragmentation pathways. In addition, the adopted investigation strategy enabled us to get a deep insight into the role played by the different fluorine content on the peculiarities of both molecular precursors and resulting CVD grown nanosystems.

Preliminary CVD growth experiments yielded high purity, single phase Mn<sub>3</sub>O<sub>4</sub> nanosystems which exhibit an appreciable absorbance in the visible range. These results pave the way to the use of these materials in a variety of technological applications, from photo-activated to gas sensing ones.

[1] L. Bigiani et al., Chem. Eur. J. 23, 17954 (2017).

ID-220

**Tailored fabrication of upside-down ZnO nanopyramid arrays: synthesis and chemico-physical characterization***C. Maccato<sup>1</sup>, D. Barreca<sup>2</sup>, T. Altantzis<sup>3</sup>, K. Kaunisto<sup>4</sup>, A. Gasparotto<sup>2</sup>*<sup>1</sup> *Università di Padova*<sup>2</sup> *Department of Chemical Sciences, Padova University and INSTM, 35131 Padova, Italy*<sup>3</sup> *EMAT, University of Antwerp, 2020 Antwerpen, Belgium*<sup>4</sup> *Department of Chemistry and Bioengineering, Tampere University of Technology, 33101 Tampere, Finland; VTT Technical Research Centre of Finland Ltd, 33101 Tampere, Finland*

ZnO, a multi-functional biosafe n-type semiconductor (EG = 3.4 eV) featuring an extremely rich variety of morphologies, has been the subject of a widespread attention thanks to its promising properties, that include a large exciton binding energy (60 meV), optical transparency, UV emission and electric conductivity. In particular, the possibility of tailoring zinc oxide chemical, physical and functional characteristics as a function of the size and shape of ZnO building blocks offers a high potential for a broad variety of applications, including (photo)catalysts, light emitting diodes and lasers, electrodes for photoelectrochemical cells, as well as nanoscale transducers, field emitters, and solid state gas sensors. Up to date, despite the huge amount of efforts dedicated to ZnO nanostructures, most of the research works have been devoted to 1D ZnO nanosystems, and the controlled fabrication of supported nanoarchitectures with precise structure and shape control may open up new directions towards the introduction of new properties and functionalities.

In the present work, porous ZnO nanopyramidal arrays with downward pointing tips and a hexagonal base were grown on Si (100) substrates by means of a catalyst-free chemical vapor deposition (CVD) process [1] starting from Zn(hfa)<sub>2</sub>TMEDA (Hhfa = 1,1,1,5,5,5-hexafluoro-2,4-pentanedione; TMEDA = N,N,N',N'-tetramethylethylenediamine) under O<sub>2</sub>+H<sub>2</sub>O atmospheres. The results obtained by a thorough chemico-physical characterization revealed the formation of high purity nanosystems, for which the preferential [001] orientation, as well as nanopyramid dimension, shape and spatial distribution, could be tailored by variations of the sole growth temperature. Basing on detailed structural analyses, we have proposed a growth model based on the combination of a direction-conducting growth and a vapor-solid (VS) mechanism, directly influenced by the adopted substrate temperature. Taken together, the results obtained in the present investigation enable to attain an enhanced control over the properties of ZnO nanopyramids grown by this technique, paving the way to subsequent research efforts aimed at the integration of the developed systems into various functional nanodevices.

[1] D. Barreca, G. Carraro, C. Maccato, T. Altantzis, K. Kaunisto, A. Gasparotto, *Crystal Growth & Design*, 2018, in press 10.1021.

## ID-310

**Solidification behaviour and mechanical properties of Al<sub>x</sub>Cu<sub>7</sub>Si ultrafine eutectic alloys with different cooling rates**

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Ternary Al-15%Cu-7%Si and Al-22%Cu-7%Si alloys specimens were generated by both transient directional (DS) and rapid solidification techniques. These techniques in combination are able to provide a very large range of cooling rates and microstructures to be correlated to each other. Overall the microstructures of the directionally solidified samples are constituted by an  $\alpha$ -Al dendritic matrix surrounded by two eutectic, that is a binary eutectic, consisting of Si and  $\alpha$ -Al, and a bimodal eutectic consisting of cellular type binary eutectic colonies ( $\alpha$ -Al + Al<sub>2</sub>Cu) in a ternary eutectic matrix consisting of ( $\alpha$ -Al + Al<sub>2</sub>Cu + Si). In the case of the Al-22%Cu-7%Si alloy, primary Si particles were also observed. A complete analysis of the dendritic length scale was performed so that relationships of primary and secondary dendritic spacing with cooling rate and growth rate could be derived. The mean dendritic spacing of the DS samples varied: from 80 to 350  $\mu\text{m}$  ( $\lambda_1$ ) / from 5 to 20  $\mu\text{m}$  ( $\lambda_2$ ) and from 90 to 250  $\mu\text{m}$  ( $\lambda_1$ ) / from 10 to 18  $\mu\text{m}$  ( $\lambda_2$ ) for the Al-15wt.%Cu-7wt.%Si and Al-22wt.%Cu-7wt.%Si, respectively. Higher tensile strengths are associated with the DS alloy containing higher copper content. Furthermore, mechanical properties have been determined for various samples related to different dendritic spacing values. The rapidly solidified microstructures were also examined which permitted the cooling rates to be estimated for such conditions.

ID-384

**Development of new Al alloys specifically designed for Additive Manufacturing***S. Marola<sup>1</sup>, D. Manfredi<sup>2</sup>, P. Konda Gokuldoss<sup>3,4</sup>, J. Eckert<sup>4,5</sup>, L. Battezzati<sup>1</sup>**<sup>1</sup> Dipartimento di Chimica, Università di Torino**<sup>2</sup> Istituto Italiano di Tecnologia, Center for Sustainable Future Technologies**<sup>3</sup> Department of Manufacturing and Civil Engineering, Norwegian University of Science and Technology**<sup>4</sup> Erich Schmid Institute of Materials Science, Austrian Academy of Sciences (ÖAW)**<sup>5</sup> Department Materials Physics, Montanuniversität*

The possibility to produce metallic objects of complex shapes by means of Additive Manufacturing (AM) has received increased attention from industries, in particular, aerospace and automotive sectors. However, up to now the materials palette available for AM processes is still limited.

In this work, preliminary investigation on the development of new alloys specifically designed for AM processes were carried out. The idea is to produce high strength nanocrystalline solids from the crystallization of Al metallic glasses [1]. Considering that in AM processes layers of material are subsequently melted according to a CAD file, the thermal profile experienced by the alloy could be exploited to obtain recrystallization directly without the need of further post processing [2]. Starting from the system proposed by Wang et al., this work is aimed at testing several Al-Transition Metal-Rare Earth alloys rapidly solidified by Melt Spinning (MS), having a cooling rate close to that of AM processes, in order to verify if these compositions are suitable for AM processes. In particular, microstructural, structural and thermal properties of the compositions under study were investigated both before and after a thermal treatment. Moreover, the processability of the alloys was evaluated through nanoindentation tests. Nano indentation was carried out because the alloy needs to be sufficiently tough to withstand the high residual stresses generated during the AM processes.

[1] Z. Wang, R.T. Qu, S. Scudino, B.A. Sun, K.G. Prashanth, D. V. Louzguine-Luzgin, M.W. Chen, Z.F. Zhang, J. Eckert, Hybrid nanostructured aluminum alloy with super-high strength, *NPG Asia Mater.* 7 (2015) 1–8. doi:10.1038/am.2015.129.

[2] E.A. Jäggle, Z. Sheng, L. Wu, L. Lu, J. Risse, A. Weisheit, D. Raabe, Precipitation Reactions in Age-Hardenable Alloys During Laser Additive Manufacturing, *Jom.* 68 (2016) 943–949. doi:10.1007/s11837-015-1764-2.

ID-392

**Formation and complex studies of InSb nanowire sheaves in anodic alumina membranes***G. Gorokh<sup>1</sup>, A. Lozovenko<sup>1</sup>, I. Obukhov<sup>2</sup>, E. Smirnova<sup>2</sup>, A. Pligovka<sup>1</sup>, A. Poznyak<sup>1</sup>**1 Belarusian State University of Informatics and Radioelectronics**2 System Recourses Ltd*

The indium antimonide possesses unique electrophysical characteristics, and one of them is small length of size quantization. If the diameter of the nanowire is less than this value, quantum-size effects appear in it. New technological approaches for the formation of such nanowires with controlled sizes are of great interest, as well as an investigation of their composition and properties. The technological foundations for the formation of InSb nanowire arrays in membranes of anodic alumina were developed. Membranes of the required thickness (30  $\mu\text{m}$ ) with pores diameter of 40 nm were created by two-step anodizing the aluminum foil in 0.2 M oxalic acid solution at potential of 37 V. A gold layer (200 nm) was deposited on the porous surface of alumina membrane to create an electrical contact. The remaining Al layer was removed in  $\text{CuCl}_2/\text{HCl}$  solution. The windows in photo resist mask  $650 \times 650 \mu\text{m}^2$  on backside were formed by photolithography. The barrier oxide layer was removed in solution of 5% phosphoric acid through photoresist mask. Electrochemical deposition of InSb was carried out in solution of  $\text{SbCl}_3$ ,  $\text{InCl}_3$  with  $\text{C}_6\text{H}_8\text{O}_7$  and  $\text{K}_3\text{C}_6\text{H}_5\text{O}_7$  (pH=1,9). Deposition was carried out at current density of 20  $\text{mA}/\text{cm}^2$  during 18 min. until the nanowires did not reach the membrane surface. Au layer 500 nm thick was deposited over the sample, and after removal of photoresist in windows the contact on the nanowire sheaves were formed. The weight ratio of elements in InSb nanostructures was determined by X-ray microanalysis: It was In -36.89% and Sb - 63,11%. Diffraction patterns shows diffuse halo in initial and annealed samples, which is the result of scattering on amorphous matrix of anodic alumina. The initial sample is predominantly amorphous, there are weak diffraction maxima corresponding to the crystalline phase of InSb (reflections on the planes (111) by  $2\theta = 23.87^\circ$  and (220) by  $2\theta = 39.66^\circ$ ) with cubic lattice and constant  $a = 6.478 \text{ \AA}$ . The current-voltage characteristics of chainlet of InSb nanowire sheaves between adjacent Au contacts were non-linear appearance, while the degree of non-linearity was different at different sites and beyond the threshold voltage was characterized by great steepness. The maximum current density through contacts, uniting  $1,1 \cdot 10^8$  quantum wires, was  $33.15 \text{ A}/\text{cm}^2$  at 3.5 V. InSb nanowire sheaves can be used to create intelligent structures, thermoelectric generators and nanorefrigerators, as well as other devices based on quantum effects.

ID-399

**Influence of iron, milling time and sintering route on microstructure and corrosion behavior in SBF medium of mechanically alloyed Ni-Ti alloys**

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This work discusses on influence of iron addition, milling time and sintering route on corrosion behavior in simulated body fluid (SBF) medium of mechanically alloyed Ni<sub>48</sub>Ti<sub>2</sub>Fe and Ni<sub>45</sub>Ti<sub>5</sub>Fe alloys (at.-%). The elemental powder mixtures were processed for different times (1, 3 and 5 h) in a planetary Fritsch P-5 ball mill under argon atmosphere using hardened steel vials and balls, rotary speed of 200 rpm, and a ball-to-powder weight ratio of 10:1. Following, the as-milled Ni-Ti-Fe powders were sintered under argon atmosphere for two different techniques: conventional pressure-less sintering (900°C for 16h) and spark plasma sintering (20 MPa at 900°C for 12 min) in order to obtain samples with 10 mm diameter. Characterization of milled powders and sintered alloys was conducted by X-ray diffraction, scanning electron microscopy, energy dispersive spectrometry, and thermal analyses. The electrochemical corrosion behavior of these alloys in 1,5% NaCl SBF medium at 36.5 °C and pH 7.4 was investigated by means of open-circuit potential (OCP) measurement and potentiodynamic polarization tests. Peaks of Ni and Ti were noted in XRD patterns of Ni-Ti-Fe powders milled for 3 and 5 h only. The particle sizes of Ni-Ti-Fe powders with rounded morphology increased during milling up to 5 h. DSC curves of as-milled Ni-Ti-Fe powders have indicated the presence of exothermic peaks owing the formation of intermetallic phases. Independently of sintering route, the microstructures of sintered Ni-Ti-Fe alloys previously milled for 5 h were mainly formed by the NiTi phase (monoclinic B'19 structure), and their martensitic transformations were close to 50 °C. The opened porosity varied between 12 and 20 % in the pressure-less sintered samples; i.e., it was lower for Fe-richer alloys and produced at longer milling times. SPS technique produced the Ni-Ti-Fe alloys with porosity lower than 2 %. The NiTi, Ni<sub>3</sub>Ti and NiTi<sub>2</sub> phases formed in the sintered Ni<sub>48</sub>Ti<sub>2</sub>Fe (Ni<sub>45</sub>Ti<sub>5</sub>Fe) alloys dissolved up to 6(10), 2(5) and 4(5) at.% Fe, which were measured by EDS analyses. The corrosion process initiated faster and the density current at the active-passive transition is higher for Ni<sub>48</sub>Ti<sub>2</sub>Fe alloy produced by conventional sintering, which can be associated to its higher porosity. Oppositely, this denser alloy produced by SPS technique exhibited lower values for passivation current density and higher corrosion potentials than the dense Ni<sub>45</sub>Ti<sub>5</sub>Fe alloy owing to its higher iron content.



ID-413

**Microstructure and corrosion behavior in SBF medium of spark plasma sintered Ti-Zr-Si-B alloys**

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*4 Universidade do Estado do Rio de Janeiro - UERJ*

Conventional Ti alloys are based on substitutional solid solutions and present good corrosion resistance in body fluid but they exhibited limited hardness and wear resistance. In this way, the use of biocompatible metal-intermetallic composites with lower friction coefficient can contribute to develop the femoral components used in hip prostheses. Previous works have indicated that the Ti-Si-B alloys can produce metal-intermetallic composites with lower friction coefficient and superior oxidation resistance while the spark plasma sintering (SPS) is used to prepare different materials with finer microstructures. This work aims to evaluate the microstructure and corrosion behavior in SBF medium of spark plasma sintered  $Ti_xZr_{20}Si_{10}B$  ( $x = 5, 7, 10, 15$  and  $20$  at.%) alloys. Metastable Ti-Zr-Si-B (at.%) powders previously prepared ball milling for 600 min were used as starting materials. SPS of mechanically alloyed Ti-Zr-Si-B powders was performed under controlled atmosphere at  $1100^\circ\text{C}$  for 12 min using 20 MPa in order to obtain cylindrical bodies with 10 mm diameter. SPS samples were characterized by X-ray diffraction, scanning electron microscopy, energy dispersive spectrometry, and Vickers hardness tests. The electrochemical corrosion behavior of these alloys in 1,5% NaCl SBF medium at  $36.5^\circ\text{C}$  and pH 7.4 was evaluated by means of open-circuit potential (OCP) measurement and potentiodynamic polarization tests. SPS technique produced dense samples with theoretical specific mass higher than 97%. Despite the short sintering time, the microstructures of the Ti-Zr-Si-B alloys were formed by Tiss (ss-solid solution) and others different intermetallic phases:  $Ti_6Si_2B$ ,  $TiB$ ,  $Ti_5Si_3$  or  $Ti_3Si$ .  $Ti_6Si_2B$  dissolving between 6 and 9.7 at. % Zr was formed in the quaternary alloys with 5 and 7 at. % Zr, respectively. In detrimental to its formation, the  $Ti_3Si$  phase was preferentially formed in the Zr-richer alloys, dissolving between 11.9 at. % Zr ( $Ti_{10}Zr_{20}Si_{10}B$ ) and 27.1 at. % Zr ( $Ti_{20}Zr_{20}Si_{10}B$ ). The Zr contents of Tiss and  $Ti_5Si_3$  in the  $Ti_5Zr_{20}Si_{10}B$  and  $Ti_{20}Zr_{20}Si_{10}B$  alloys varied between 4.3-15.1 and 9.7-15.2 at. %, respectively. SPS Ti-Zr-Si-B samples presented Vickers hardness values between 900 HV and 1500 HV, which were less pronounced for Zr-richer alloys owing mainly the higher amounts of Tiss in their microstructures. SPS Ti-Zr-Si-B alloys exhibited superior corrosion resistance in SBF medium and hardness values than the conventional  $Ti_6Al_4V$  alloy.

Thursday 5 July afternoon - 17:30/18:30

Poster session 4  
**PHASE TRANSFORMATION**  
D. Mirabile Gattia

ID-35

**Microstructure evolution and mechanical property of repair welded  $\text{Cu}_{7.0}\text{Ni}_{1.75}\text{Si}_{0.5}\text{Cr}$  alloy***H.S. Yeh, H.S. Wang, H.G. Chen, J.J. Wu, J.J. Liu, P.W. Liu**Department of Materials Science and Engineering, I-Shou University*

Considering its advantages of high tensile strength and high thermal conductivity,  $\text{Cu}_{7.0}\text{Ni}_{1.75}\text{Si}_{0.5}\text{Cr}$  alloys show good prospects as substitutes for the toxic Be-Cu alloy. However, due to its high thermal conductivity, such an alloy becomes difficult welded material for the repair welding. An earlier study suggested that the solid solution heat treatment can help reduce its thermal conductivity and enhance its weldability. Therefore, this study repair welded  $\text{Cu}-7.0\text{Ni}-1.75\text{Si}-0.5\text{Cr}$  samples, including with and without pre-weld heat treated samples (solid solution heat treatment only), using the gas tungsten arc welding (GTAW) process with a variety of welding parameters. After repair welding, those welds were post-weld heat treated (PWHT) (including solid solution and aging heat treatment). The microstructure, mechanical properties, and thermal properties of the pre-weld heat-treated, repair-welded, and PWHT samples were then investigated and compared. The test results show that a proper pre-weld heat treatment obtains a deeper penetration and unified shape of the repair weld. The large sizes of the Ni/Si and Cr/Si compounds in the pre-weld heat-treated samples were turned into continuous precipitation phases (mainly of the Ni/Si compound) along the grain boundaries in the weld fusion zone (WFZ), which may have harmful effects on the mechanical properties. Hardness in the heat affected zone (HAZ) of the repair weld dropped, caused by grain growth and partial heat treatment in this area. However, after PWHT, a continuous precipitation phase along the grain boundaries in the weld was hardly observed. Furthermore, the hardness values in the parent material, HAZ, and WFZ are similar and substantially enhanced, attributed to the nano-sized Ni/Si phase that was re-precipitated in those zones.

ID-71

**Additional arguments in favour of the phenomenon of electrochemical phase formation in metals via a supercooled liquid state stage**

O. Girin

*Ukrainian State University of Chemical Technology*

A previously unknown phenomenon of electrochemical phase formation in metals via a supercooled liquid state stage was established quite recently. Essentially, this phenomenon is to be understood as follows: during metal electrodeposition onto a solid cathode in an aqueous environment, a deeply supercooled metal liquid evolves in the form of multiple liquid atomic clusters avalanching at various sites near the cathode or the growing deposit and solidifies ultra-rapidly at the deposition temperature.

The present research aimed to characterize the features of structure and phases in electrodeposited metals that argue for electrochemical phase formation through emergence and rapid solidification of a deeply supercooled metallic liquid.

The principal hypothesis underlying the experimentation was that metastable phases and/or structures must be present in the electrodeposits if the phenomenon of electrochemical phase formation in metals via a supercooled liquid state stage indeed occurs. Such metastable phases and structures would be intermediate products of phase transformations from a metallic liquid having an amorphous structure to a solid deposited metal with a crystalline structure. First of all, one should expect to reveal in those metals such metastable arrangements and/or phases like amorphous or quasicrystalline structures and metastable polymorphs.

The phenomenon of electrochemical phase formation in metals via a supercooled liquid state stage has received additional proofs based on the following experimental facts:

- electrochemical phase formation under conditions hindering crystallization yields metals with amorphous structure typical of solidified metallic liquid;
- occurrence of spherulites and quasicrystals in electroplate layers next to the cathode, a behaviour similar to that in interface-near metal layers at crucible walls in ultrarapid solidification of a deeply supercooled melt;
- electrochemical phase formation in metals resulting in phases with quasicrystalline structure when formation of a periodically ordered crystal structure is hindered in the course of deposition;
- electrochemical phase formation of polymorphous metals produces metastable modifications typical of entities that crystallized from a liquid state at extremely high rates.
- obedience to a distinct orientation relationship between grains of the stable and the metastable phase, which is typical of phase transformations proceeding at extremely high rates.

ID-89

**Room-temperature mechanochemical synthesis of WC and Mo<sub>2</sub>C carbides***O. Nakonechna, M. Dashevskiy, N. Belyavina**Taras Shevchenko National university of Kyiv*

Due to its extremely hardness, high abrasion resistance and strength the WC monocarbide is the most important one widely used in making materials for abrasive and metal cutting tools. Moreover, in refractory alloys the Mo<sub>2</sub>C carbides like WC are used as a minor constituent to act as dispersion strengtheners. Traditionally, manufacturing of these carbides is based on a high-temperature (1300- 2300 °C) direct reaction of metal or metal oxide with carbon or carbon-containing gas. In this work, WC and Mo<sub>2</sub>C carbides have been synthesized from the elemental metal powder and the carbon nanotubes (CNTs) by mechanical alloying in a high energy planetary ball mill. Hardened stainless steel balls and a vial with a ball-to-powder weight ratio of 20:1 were used.

Four hours processing of initial charges results in a formation of the high temperature W<sub>2</sub>C and Mo<sub>2</sub>C carbides. XRD study has revealed that the suitable model for description of the crystal structure of both carbides is the ζ-Fe<sub>2</sub>N-type (space group P-31m; a = 0.5168(3), c = 0.4710(4) for W<sub>2</sub>C and a = 0.5174(3), c = 0.4744(4) for Mo<sub>2</sub>C) with vacancies in the metal sublattice. At this, the calculated carbon contents (of ≈ 35 at. % C for W<sub>2</sub>C and of ≈ 38 at. % C for Mo<sub>2</sub>C) are inherent to the carbon-rich sides of solid solutions based on the high temperature Me<sub>2</sub>C carbides. Further processing (up to 10 h) results in a gradual W<sub>2</sub>C + CNT → WC transformation and grinding of Mo<sub>2</sub>C particles, which are accompanied by the wear debris leading to formation of the cubic W<sub>6</sub>Fe<sub>6</sub>C or Mo<sub>3</sub>Fe<sub>3</sub>C carbides with a = 1.093(1) nm and a = 1.113(1) nm, respectively. Moreover, the amount of these additions gradually increases with processing time increasing. Grain size values for Me<sub>2</sub>C carbides estimated by the Williamson–Hall plots are equal to 4 nm for WC and 12 nm for Mo<sub>2</sub>C.

Thus, the room temperature synthesis of the nanoscaled WC and Mo<sub>2</sub>C carbides (Mo<sub>2-x</sub>C, indeed) have been successfully performed from the mixture of powder metals and CNTs in a high energy planetary ball mill. It is the use of CNTs in the synthesis process that makes it more efficient since essentially reduces its duration.

ID-111

**Phase transformation and morphology evolution of  $\text{Ti}_{50}\text{Cu}_{25}(\text{Ni}_{80}\text{Sn}_{20})_{25}$  during mechanical milling**

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Nanocrystalline/amorphous powder was produced by ball milling of  $\text{Ti}_{50}\text{Cu}_{25}(\text{Ni}_{80}\text{Sn}_{20})_{25}$  master alloy. Both laser diffraction particle size analyzer and scanning electron microscope (SEM) were used to monitor the change in particle size as well as a shape of particles as a function of milling time. During ball milling the mean particle size decreased with milling time to  $\sim 38 \mu\text{m}$  after 180 min of milling time. The deformation-induced hardening and phase transformation caused the hardness value increase from 506 to 779 HV. XRD analysis was used to observe the change in phases/amorphous content as a function of milling time. The amount of amorphous fraction increased continuously until 120 min milling time (35 wt% amorphous content). The interval of crystallite size is between 1 and 10 nm after 180 min of milling time with 25 wt% amorphous fractions.

ID-112

**Ti<sub>50</sub>Cu<sub>25</sub>(Ni<sub>80</sub>Sn<sub>20</sub>)<sub>25</sub> amorphous/nanocrystalline powder produced by milling under -78 °C**

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Ti<sub>50</sub>Cu<sub>25</sub>(Ni<sub>80</sub>Sn<sub>20</sub>)<sub>25</sub> amorphous/ nanocrystalline powder was produced by ball milling. Crystalline master alloys were prepared by induction melting under purified argon atmosphere.

During the mechanical amorphization the grinded ingots were milled for different durations of time and with several interruptions in order to analyse the structure of the powders. The mechanical milling was performed in a Pulverisette5 high energy planetary ball-mill under argon atmosphere using stainless vial and balls. The stainless vial was cooled with dry ice under the ball milling. The ball-to-powder ratio was 80:1. The milled powders were analyzed by XRD to determine the amorphous fraction and observed changes in the phases/amorphous content as function of milling time. The scanning electron microscope (SEM) were analysed the changes in the particle size as well as in the shape of particles as a function of milling time.

The amount of amorphous fraction increased continuously until 120 min milling time (33 wt% amorphous content). The interval of crystallite size is between 2 and 15 nm after 180 min of milling time with 33 wt % amorphous fractions.

ID-142

**Microstructure, mechanical properties and texture evolution of cold rolled and annealed  $\text{Ti}_{29}\text{Nb}_2\text{Mo}_6\text{Zr}$  titanium alloy for orthopedic application***A. R. Vieira Nunes<sup>1</sup>, L. S. Araujo<sup>1</sup>, S. Borborema<sup>2</sup>, L. Malet<sup>3</sup>, J. Dille<sup>3</sup>, C. A. Nunes<sup>4</sup>, L. H. de Almeida<sup>1</sup>*<sup>1</sup> UFRJ<sup>2</sup> UERJ<sup>3</sup> ULB<sup>4</sup> USP

A low Young's modulus is required for titanium alloys used in orthopedic implants, such as hip prosthetic stems, in order to avoid stress shielding due to a large difference in Young's modulus between the prosthetic stem and the cortical bone. The low Young's modulus has been observed to occur in metastable  $\beta$  Ti alloys by precipitation stress-induced  $\alpha''$  martensite during cold rolling through the preferred texture development of  $\langle 010 \rangle \alpha''$  and  $\langle 110 \rangle \beta$  along the rolling direction. Under this context, this work presents the relationship between cold deformation on the microstructure of  $\beta$  metastable  $\text{Ti}_{29}\text{Nb}_2\text{Mo}_6\text{Zr}$  alloy, as well as the influence of the degree of cold rolling on Young's modulus, after homogenization and annealing heat treatments. The ingots were produced by arc melting under high purity argon atmosphere and were solution treated at 1000 °C under high vacuum for 24 h, followed by quenching in water at room temperature, and the samples were cold rolled to reduce its thickness up to 90% and annealed at 950°C for 1h. The microstructural evolution was characterized by optical and transmission electron microscopy, and X-ray diffraction. The mechanical properties were investigated by nanoindentation and microhardness. The electron backscattering diffraction and Schmid factor analysis were used to study of the texture evolution after annealing and the presence of twinning systems. The  $\text{Ti}_{29}\text{Nb}_2\text{Mo}_6\text{Zr}$  alloy presents equiaxed  $\beta$  grains after solution heat treatment. The grains elongated gradually with increasing deformation, inducing the precipitation of  $\alpha''$  martensite. Two twinning systems,  $\{112\} \langle 111 \rangle$  and  $\{332\} \langle 113 \rangle$ , were observed. The hardness of the samples increased with the degree of deformation, while elastic modulus decreased. But the annealed samples showed higher hardness and Young's modulus than cold rolled samples. The cold rolled  $\beta$  Ti-Nb-Mo-Zr alloy at 90% maximized hardness/Young's modulus ratio in all conditions, being a potential candidate to use as orthopedic implants.



ID-143

**Ni-based metallic glass composites containing Cu-rich crystalline nanospheres***J. He<sup>1</sup>, Y. Xi, X. Sun, I. Kaban<sup>2</sup>*<sup>1</sup> *Institute of Metal Research, Chinese Academy of Sciences*<sup>2</sup> *IFW Dresden, Institute for Complex Materials*

The synthesis of metallic glass matrix composites by using phase separation phenomena has attracted great attention to develop in situ crystalline/amorphous and amorphous/amorphous composites exhibiting unique soft magnetic and mechanical properties. Recently, the crystalline/amorphous composite was developed on the basis of some immiscible systems such as Al-Pb alloy with stable miscibility gap and Fe-Cu alloy with metastable miscibility gap. The phase-separation microstructure is attributed to the immiscible system with large positive heat of mixing. As it was known, the crystalline copper and nickel have the same crystal structure, similar atomic radius and electronegativity. The binary Ni-Cu alloy is a typical isomorphous system, exhibiting complete liquid and solid solubility without compounds. The heat of mixing between nickel and copper is positive, i.e. +4 kJ/mol. It was indicated that there exists a solid-state miscibility gap in the Ni-Cu binary system at a temperature somewhere between 450 K and 923 K. However, the liquid-state miscibility gap was not detected by the measurements of electrical resistivity and magnetic susceptibility. No information is available in the literature about the design of the crystalline/amorphous composite based on the isomorphous Ni-Cu system so far.

Based on the Ni-Cu alloy, in this work a quaternary Ni-Cu-Nb-Ta system has been designed to obtain composite microstructure with spherical crystalline Cu-rich particles embedded in amorphous Ni-rich matrix. The alloy samples were prepared through using single-roller melting-spinning method. The microstructure and thermal properties of the as-quenched alloy samples were characterized. It shows the occurrence of the liquid-liquid phase separation into two coexistent Cu-rich and Ni-rich liquids. With the decrease of the temperature, the content of the component Cu in the Ni-rich liquid matrix continuously reduce. Under the condition of the rapid solidification, the Cu-rich droplets begin to freeze at about 1369 K, and the Ni-rich liquid matrix undergoes a liquid-to-glass transition at about 900 K. Consequently, it results in the composite microstructure with the Cu-rich crystalline particles embedded in the Ni-rich glassy matrix. The average size of the Cu-rich particles is strongly dependent upon the Cu content. The effect of the alloy composition on the behavior of liquid-liquid phase separation and microstructure formation has been discussed.

ID-265

**Understanding correlation between mechanical property and color change of  $\text{Cu}_{100-x}(\text{AlNi})_x$  alloys***S. Y. Choi<sup>1</sup>, S. C. Mun<sup>1</sup>, K. B. Kim<sup>1</sup>, Y. B. Jeong<sup>1</sup>, H. J. Park<sup>1</sup>, Y. S. Kim<sup>1</sup>, S. H. Hong<sup>1</sup>, S. W. Park<sup>1</sup>, S. J. Kwon<sup>1</sup>*<sup>1</sup> *Sejong University*

Until now, the color of metals is usually limited to control the secondary process such as covering organic solvent and anodizing process. It has problems in which surface of material was peeled off or color was coated irregular, since the bondability between the two type of interfaces is unstable. Leading to disadvantage that durability of color is decreased. To overcome these problems, recent studies have been focused on designing alloy composition to define color of metal. One of noticeable representative color alloys is Cu alloy, it is that color is changed by controlling the transition energy through the effects of addition elements. However, In the case of color change using the transition energy, the solid solution was required and limitation of solubility was generated. For these reasons, selection of composition was limited, so it can hardly control the mechanical property and the variation of color. Recently, in order to overcome these problems, precipitation of intermetallic compounds having a specific color is being studied by using alloy design. As mentioned above, when precipitation of intermetallic compounds was controlled, it is possible to easily control mechanical property and color.

Because of this, In this study, the changing of color and improving the mechanical property of  $\text{Cu}_{100-x}(\text{AlNi})_x$  alloys were investigated by controlling precipitation of AlNi intermetallic compound. According to previous study, color of AlNi intermetallic compound was described as blue, so we used to easily measure changing of color by following this theory. The color of the alloy was determined by spectrometer. The color difference was expressed by the CIE Lab\* color coordinate system. X-ray diffraction (XRD) was performed for structural characterization. Microstructure of the as-cast samples was analyzed by scanning electron microscopy (SEM). Mechanical property of these alloys was measured by Micro-Indentation. Based on these results, the relationship between changing of color and mechanical property of  $\text{Cu}_{100-x}(\text{AlNi})_x$  alloy was discussed with precipitation phase control.

ID-267

**Investigation on the relationship of the microstructure and mechanical properties by Mn addition in the Ti-Cr-Mn alloys***S. W. Park, K. B. Kim<sup>1</sup>, S. H. Hong, S. C. Mun, Y. S. Kim, H. J. Park, S. J. Kwon, S. Y. Choi*<sup>1</sup>*Sejong University*

From the past, Ti based alloys are very interesting and promising materials for good properties such as their light weight, excellent mechanical properties and high corrosion resistance. Among these alloys,  $\beta$ -Ti alloys have been studied with interest due to their characteristics. Like other alloys, the characteristic of Ti-alloys is determined by microstructures (i.e. morphology, grain size, formed phase, etc.). Adding minor alloying elements is representative method to control the microstructure of alloys. Especially, Cr and Mn are known as  $\beta$ -Ti phase stabilizing elements to obtain high fraction of  $\beta$  phase. Ti-Cr binary alloys have high strength due to solution strengthening effect by wide solid solution region. Furthermore, these alloys show high ductility because they have many slip bands during deformation. However, some improvements of properties to use commercially are required. Ti-Cr binary alloys having around 5 at.% Cr form unstable  $\beta$ -Ti phases,  $\omega$ -Ti and  $\alpha''$  Ti phases simultaneously because it is difficult to completely stabilize the  $\beta$ -Ti phase. These  $\omega$  and  $\alpha''$ -Ti play a role to strengthen the alloy to get high strength but it causes the decrease of elongation.

In this study, Mn was added in Ti-Cr binary alloy with low contents of Cr to improve a weak ductility. Also, it was investigated that the behavior and relationship of microstructures and mechanical properties by the chemical composition difference of alloys. The phase and microstructure of alloys were analyzed by XRD (X-Ray Diffraction) and SEM (Scanning Electron Microscope), respectively. Finally, the compressive testing was conducted to measure mechanical properties using UTM (Universal Testing Machine) at room temperature.

ID-269

**Surface functionalization on porous  $\text{Al}_{88}\text{Cu}_6\text{Si}_6$  alloy via two-step hybrid processes***H. J. Park, K. B. Kim, Y. S. Kim, S. C. Mun, S. Y. Choi, S. J. Kwon, S. W. Park**Sejong University*

Functionalization of structural materials has been attempted by dealloying and hydrothermal process. Nanostructure-dendrite composite,  $\text{Al}_{88}\text{Cu}_6\text{Si}_6$ , was used and selective dissolution as dealloying could remove only micron-scale  $\alpha$ -Al dendrite from the matrix, then surface porous  $\text{Al}_{88}\text{Cu}_6\text{Si}_6$  alloy with well-formed skeletal structure was prepared. The micron-scale  $\alpha$ -Al dendrites turned into open pores and the size range of it was from 5  $\mu\text{m}$  to 10  $\mu\text{m}$ . Hydrothermal process was used to grow  $\text{Al}_2\text{O}_3$  as functional oxides and the oxides growth up to 3  $\mu\text{m}$ . The size of oxides increased and stabilized like single crystal as hydrothermal method proceeded longer.

ID-290

**Preparation of spherical TaNbHfZrTi high entropy alloy powder by hydrogenation-dehydrogenation reaction and thermal plasma treatment***J. M. Park<sup>1</sup>, K. B. Park<sup>1</sup>, S. M. Yang<sup>1</sup>, J. W. Kang<sup>1</sup>, T. W. Lee<sup>1</sup>, K. Park<sup>1</sup>, T. W. Na<sup>1</sup>, H. K. Park<sup>1</sup>**<sup>1</sup> Korea Institute of Industrial Technology*

TaNbHfZrTi high entropy alloy (HEA) powders were fabricated by hydrogenation-dehydrogenation reaction and thermal plasma treatment. TaNbHfZrTi HEA ingot was prepared by vacuum arc remelting and it was annealed in the hydrogen atmosphere. After annealing, the HEA was phase-transformed to brittle hydrides and they were pulverized by ball-milling. The hydride powders were annealed in the vacuum furnace and the HEA powders were formed by dehydrogenation reaction. The HEA powders fabricated by hydrogenation-dehydrogenation reaction had an irregular shape and they were spheroidized by inductively coupled thermal plasma treatment. By this process spherical TaNbHfZrTi HEA powders could be successfully fabricated.

ID-314

**Effect of cyclic heat treatment on commercially pure titanium part fabricated by electron beam additive manufacturing***H. K. Park<sup>1</sup>, T. W. Na<sup>1</sup>, J. M. Park<sup>1</sup>, Y. Kim<sup>1</sup>, G. H. Kim<sup>1</sup>, B. S. Lee<sup>1</sup>, H. G. Kim<sup>1</sup>**<sup>1</sup> Korea Institute of Industrial Technology*

Commercially pure titanium (CP-Ti) is generally used for medical industry cause its biocompatibility and mechanical properties. Recently, with development of additive manufacturing technology, the study on the patient-specific orthopedic implant has been widely conducted. In particular, electron beam additive manufacturing (EBAM) exhibits high strength with the martensitic phase due to rapid melting and solidification. However, it could have an anisotropic property along with the building direction and higher elastic modulus than human bone. Thus, to improve the reliability and functionality of medical CP-Ti part fabricated by EBAM, we studied a post-treatment like cyclic heat treatment. For uniform microstructure by inducing the repetitive nucleation during phase transformation, the specimens were repeatedly heat-treated from 25°C to 1,000°C in Ar atmosphere. Microstructural and mechanical studies were carried out with as-built specimen and heat-treated specimens for 1, 3, and 5 cycles. Grain size was uniformly refined from 61.2 μm to 19.4 μm, in addition the elastic modulus was lowered from 136.8 GPa to 64.4 GPa. Although the yield and tensile strength were slightly decreased after cyclic heat treatment, it was still higher value compared with the wrought CP-Ti part. For the patient-specific CP-Ti part, consequently, the cyclic heat treatment could be considerable post-process without any mechanical process.

ID-328

**Study on the effect of boron on the mechanical properties of FCC high entropy alloys***J. S. Lee<sup>1</sup>, K. N. Yoon<sup>1</sup>, H. Oh<sup>2</sup>, S. J. Kim<sup>1</sup>, E. S. Park<sup>1</sup>*<sup>1</sup> *Seoul National University*<sup>2</sup> *Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University*

Boron is a small-sized element added to various types of alloys such as stainless steels, titanium, and superalloys for microstructure & grain size modification, enhancement of creep & wear resistance, and ductility. The precipitation of boride causes increased hardness and wear resistance of the alloys. Recently, the boron added austenitic stainless steels exhibited better high temperature mechanical properties due to the suppression of creep cavitation through boron segregation. Nonetheless, very few reports on the studies of the effect of boron addition in the recently developed high entropy alloys (HEAs) have been made, although HEAs show a potential application in various temperature ranges with excellent mechanical properties. Therefore, in the present study, the effect of low boron concentration in transformation induced plasticity (TRIP) exhibiting FCC HEAs was studied. Indentation, tensile test, characterization and electron microscopy techniques were employed to the boron added alloys. As a result, we report retained TRIP effect along with improved strength and ductility. Property manipulation of HEAs through the addition of interstitial elements other than conventionally utilized carbon and nitrogen can lead to optimized properties in the desired direction ultimately leading to the better applicability of the alloys.

ID-338

**Investigation of the effect of hot rolling process on the microstructure and mechanical properties of Cu-Mn alloys***S. J. Kwon, S. C. Mun, K. B. Kim, S. Y. Choi, S. W. Park, Y. B. Jeong, H. J. Park, Y. S. Kim, S. H. Hong**Sejong University*

Cu alloy is a main material of electric device industry because of its good corrosion resistance, wear resistance and superior electrical conductivity. In accordance with the miniaturization of electronic equipment, it is necessary to improve not only the electrical conductivity but the mechanical properties of Cu alloys for the various applications. Cu-Mn alloys with high manganese content have a single phase face-centered cubic (FCC) structure in high temperature. The manganese phase is precipitated during the cooling process relying on a solubility with temperature. In this way, the mechanical properties of Cu alloys can be improved with work hardening and phase control by rolling and heat treatment.

In this study, we researched the relation of the microstructure and mechanical properties of as-cast and rolled Cu-Mn alloys. Also, we confirmed its mechanical deformation behavior depending on the manganese content. The microstructure and phase analysis were examined by using Scanning electron microscope (SEM) and X-ray Diffraction (XRD). Mechanical properties were measured by Universal Testing Machine (UTM) and micro indenter. From these results, we researched the changes of the microstructure and mechanical properties of Cu-Mn alloys after rolling and heat treatment depending on manganese content.



ID-376

**Effect of composition and milling time on microstructure and Vickers hardness of mechanically alloyed and spark plasma sintered  $(67-x)\text{Ti}_x\text{Zn}_{22}\text{Si}_{11}\text{B}$  ( $x=2$  and  $6$  at.%) alloys**

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<sup>4</sup> Universidade de São Paulo

<sup>5</sup> Universidade do Estado do Rio de Janeiro

The present work reports on effect of zinc addition (2 and 6 at.-%) and milling time on microstructure and Vickers hardness of mechanically alloyed and spark plasma sintered  $(66,7-x)\text{Ti}_x\text{Zn}_{22}\text{Si}_{11}\text{B}$  alloys (at.-%). Ball milling at different times (20, 60, 180 and 300 min) was conducted under argon atmosphere in a planetary Fritsch P-5 ball mill using WC-6Co vial (225 mL) and balls (10 mm de diameter), rotary speed of 300 rpm and a ball-to-powder weight ratio of 10:1. Cylinder bodies with 10 mm diameter were consolidated by spark plasma sintering (1100°C, 12 min, 20 MPa) under argon atmosphere. As-milled powders and sintered samples of Ti-Zn-Si-B were evaluated by X-ray diffraction (XRD), scanning electron microscopy (SEM), dispersive energy spectrometry (EDS), laser diffraction particle size analysis, and Vickers tests. It was noted a similar behavior during ball milling of Ti-Zn-Si-B powder mixtures. Only the peaks of alpha-Ti and Si were indexed in XRD patterns of Ti-Zn-Si-B powders milled for 300 min. Rietveld refining indicated that the amount of amorphous structures was increased during milling up to 300 min, which was more pronounced for the  $\text{Ti}_6\text{Zn}_{22}\text{Si}_{11}\text{B}$  powders. The particle sizes of the  $\text{Ti}_2\text{Zn}_{22}\text{Si}_{11}\text{B}$  and  $\text{Ti}_6\text{Zn}_{22}\text{Si}_{11}\text{B}$  powder mixtures increased during milling from 94 (20 min) to 156 (300 min) micrometers and from 101 (20 min) to 136 (300 min) micrometers, respectively. Coherently, the average specific surface area of powder particles was continuously reduced during milling. Despite the adopted parameters, the spark plasma sintering produced dense  $\text{Ti}_x\text{Zn}_{22}\text{Si}_{11}\text{B}$  ( $x = 2$  and  $6$  at.-%) alloys with 98% from their theoretical specific mass. Regardless of milling time, the amount of  $\text{Ti}_6\text{Si}_2\text{B}$  was reduced in microstructure of the spark plasma sintered  $\text{Ti}_6\text{Zn}_{22}\text{Si}_{11}\text{B}$  alloy. EDS analysis indicated that the  $\text{Ti}_6\text{Si}_2\text{B}$  phase dissolved close to 1 at.-% Zn. Beside the TiB and  $\text{Ti}_5\text{Si}_3$ , other zinc-rich unknown phase was also found in microstructure of the sintered Ti-Zn-Si-B alloys. Depending on milling time, the average Vickers hardness values of the  $\text{Ti}_2\text{Zn}_{22}\text{Si}_{11}\text{B}$  and  $\text{Ti}_6\text{Zn}_{22}\text{Si}_{11}\text{B}$  alloys varied between 1060-1088 HV and 970-1036 HV, respectively.

ID-414

**Ab initio investigation of Fe-Ge alloys***M. Matyunina<sup>1</sup>, M. Zagrebin<sup>1</sup>, V. Sokolovskiy<sup>1</sup>, V. Buchelnikov<sup>1</sup>*<sup>1</sup>*Chelyabinsk State University*

Intermetallic iron-rich compounds Fe-X (X =Ga, Ge, Al) are interesting because of their owing unusual mechanical, magnetic and electrical properties, for instance, significant magnetostrictive properties [1-4]. Fe-Ge alloys are less studied as compared with Fe-Ga and Fe-Al alloys. The magnetostriction of Fe<sub>100-x</sub>Ge<sub>x</sub> alloys is very sensitive to the structure present in the samples [2]. Experimental investigation of Fe<sub>75</sub>Ge<sub>25</sub> alloys shows the transforms from the face-centered cubic phase (L12) to the hexagonal phase (D019) on heating above 923 K [5].

This work presents the results of ab initio investigations of the structural and magnetic properties of Fe<sub>100-x</sub>Ge<sub>x</sub> alloys (0≤x≤31.25) with the help of density functional theory, implemented into Vienna Ab initio Simulation package [6, 7]. The structural optimization of crystal lattices A2 (Im $\bar{3}$ m), L12 (P m $\bar{3}$ m), D03 (F m $\bar{3}$ m) and D019 (P 63/mmc) phases of Fe-Ge alloys was performed using the generalized gradient approximation in Perdew-Burke-Ernzerhof parametrization [8] with an account of supercell approach (32 atoms in supercell). The tetragonal shear modulus was calculated for each of considered phases.

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ID-459

**Solidification microstructures in an undercooled eutectic Co-Si alloy***G. Fiore, A. Quaglia, L. Battezzati**Dipartimento di Chimica - Università di Torino*

Results on solidification of the compound-compound eutectic Co-Si61.8 at.% alloy under various containerless processing conditions and different undercooling values have been previously reported [1, 2]. These experiments show that the microstructure of the samples strongly depends on undercooling with sharp transition from single to double thermal events. Complex microstructures distributed in sample zones are formed due to phase selection and delay times.

In the present work, an alloy with the same composition has been solidified by mean of three different techniques, melt spinning, copper mould casting and conventional cooling in a calorimeter cell, which allow to access a wide range of undercooling levels. The microstructures (phase constitution, morphology and crystal size) are compared in order to evaluate the role of nucleants and possible catalytic intermediates in solidification.

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[2] Y. K. Zhang, *Acta Mater.*, 61 (2013) 4861.

ID-478

**Phase transformation in Nb-modified Ti-5553 alloy during aging heat treatments***V. Carvalho Opini, M. Gerardi de Mello, R. Caram**University of Campinas*

The need for materials with enhanced mechanical performance has resulted in the design of new metastable beta Ti alloys, which are able to retain the beta BCC phase at room temperature. Usually, beta phase in Ti alloys is soft and present limited mechanical strength. Aging heat treatments of beta titanium alloys make possible to tailor the microstructure and consequently, their mechanical behavior. Therefore, it is essential to understand in details the solid state transformation and hence, the sequence of phase transformation. This investigation aims to discuss phase transformation of an Nb-modified beta Ti-5553 alloy during aging heat treatments. Nb-modified Ti-5553 ingots were arc melted, hot swaged and heat treated using different aging procedures. Samples were characterization by using high temperature X-ray diffraction, differential thermal analysis, scanning electron microscopy, transmission electron microscopy, measurements of the elastic modulus and Vickers hardness. The results obtained showed that aged Nb-modified Ti-5553 samples present high tensile strength, reasonable ductility and reduced phase transformation kinetics.

Thursday 5 July afternoon - 17:30/18:30

Poster session 4  
**CERAMIC MATERIALS**  
D. Mirabile Gattia

ID-84

**Thermoluminescent respond of quantum dots in borate glasses***M. Vallejo, P. Ceron, C. Gomez, R. Navarro, M. Sosa**Universidad de Guanajuato*

Borate glasses doped with  $Dy^{3+}$  ions, silver nanoparticles (SNPs) and containing Quantum Dots were synthesized in the present work. We report photoluminescence characterization by absorption and emission spectra. The effect of Quantum Dots on the thermoluminescence (TL) glow curves was studied. The scanning electron microscopy (SEM) shows the Quantum Dots in the matrix glass. Absorption spectra of the samples show the influence of the Quantum Dots and SNP in the bands 350 nm at 425 nm associated with the  $Dy^{3+}$ , in the same spectra we can see the bands 750, 800, 875, 1098, 1278 nm and 1675 nm belonging to the  $Dy^{3+}$ . Emission spectra show two prominent bands at 480 nm and 574 nm and one faint band at 665 nm corresponding to  $4F9/2 \rightarrow 6H15/2$ ,  $4F9/2 \rightarrow 6H13/2$  and  $4F9/2 \rightarrow 6H11/2$  transitions, respectively. All bands under 364 nm pumping, and the fluorescence in the 550 nm and 590 nm spectral range enhanced. The photostability of the samples was also studied in the UVA (315–403 nm) and UVB (280–315 nm) ranges. TL due to ultraviolet radiation (UVR) was studied; the glow curves show significant dependence of the TL intensity with the increment of SNPs and Quantum Dots in the samples. These results show the Borate glasses doped with  $Dy^{3+}$  containing SNP and Quantum Dots as a potential candidate to be use in solid-state illumination and retrospective dosimetry.

ID-103

## Characterization of Algerian DD3 Kaolin

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<sup>2</sup> Laboratoire de Magnétisme et Spectroscopies des Solides (LM2S), Université Badji Mokhtar, Annaba

The objective of this work is a structural and microstructural characterization of Algerian kaolin in order to valorize these local raw materials, and to elaborate of refractory bricks from DD3 kaolin. The DD3 kaolin of Djebel Debbagh-Guelma located in the North-East of Algeria has been characterized by means of X-ray diffraction (XRD), scanning electronic microscopy (SEM) and thermal analysis (DTA/TGA). The hydrothermal rock contains mainly 41% silica, 35% alumina, 17% of fire mass and small amounts of MnO, CaO and Fe<sub>2</sub>O<sub>3</sub>. X-ray analysis of DD3 kaolin shows the presence of the clay minerals which are kaolinite or halloysite as main phases as well as the minor phases of muscovite and todorokite. Differential thermal analysis scan reveals the existence of several endothermic and exothermic peaks in the temperature range (50-1000)°C. The first endothermic peak at about 80°C can be attributed to the release of interstitial water in the kaolinite [2SiO<sub>2</sub> Al<sub>2</sub>O<sub>3</sub> 2H<sub>2</sub>O]. The dehydroxylation to metakaolinite (Al<sub>2</sub>O<sub>3</sub> 2SiO<sub>2</sub>) occurs between 400 and 500°C. The exothermic peak at 995°C can be ascribed to the metakaolinite restructuring. The thermo-gravimetric analysis curve shows that the mass loss between 400 and 800°C is about 14%. The SEM observations show a needle-like form structure with an entanglement in all the directions of the halloysite.

ID-198

**Influence of powders morphology and standoff distance on the microstructure of  $\text{Cr}_3\text{C}_2$ -Ni20Cr cold sprayed coatings***A. Góral<sup>1</sup>, W. Żórawski<sup>2</sup>, M. Makrenek<sup>2</sup>, S. Kowalski<sup>2</sup>**<sup>1</sup>Institute of Metallurgy and Materials Science, Polish Academy of Sciences**<sup>2</sup>Kielce University of Technology*

Cermet coatings consisting of hard reinforcing phase embedded in a tougher matrix achieve a wide spectrum of improved properties. Recently, a cold spray technology has become capable of manufacturing cermet coatings. By applying of this technology, the deleterious effects of oxidation, phase transformation, decomposition, grain growth and other problems inherent to conventional thermal spray techniques can be minimized. The paper presents the influence of the powders morphology and standoff distance on the microstructure (phase composition, porosity), surface topography and mechanical properties (micro- and nanohardness, Young's modulus) of the  $\text{Cr}_3\text{C}_2$ -25(Ni20Cr) coatings.  $\text{Cr}_3\text{C}_2$ -25(Ni20Cr) coatings were sprayed on the Al 7075 alloy by means of cold spray system Impact Innovations 5/8 with robot Fanuc M-20iA and positioner ZAP ROBOTYKA using two commercial powders. Powders differ in their morphology and grains size distribution. Scanning electron microscopy and X-ray diffraction investigations of the as-sprayed coatings did not show the phase transformation during cold spray deposition and the original morphology of the submicron particles was unchanged. The  $\text{Cr}_3\text{C}_2$  carbide particles are mainly distributed between plastically deformed and elongated nickel-chromium matrix grains. The particles appear to be tightly bonded, and there is a little porosity of the coatings. There are no discontinuities and microcracks at the interface between the substrate and the deposited coatings. The  $\text{Cr}_3\text{C}_2$ -25(Ni20Cr) coatings significantly differ in the surface roughness.

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ID-337

## Synthesis and properties of ATZ ceramic composite obtained by mechanical alloying

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In this study, alumina-toughened zirconia composite (ATZ), was developed, starting the powder mixture obtained by mechanical alloying (MA). The  $ZrO_2(3mol\%Y_2O_3)$ , with 20 wt% of  $Al_2O_3$  was synthesized by 1-60h mechanical alloying (MA) in a planetary ball mill under argon atmosphere, using a rotary speed of 200 rpm, a ball-to-powder weight ratio of 10:1. Powders milled were then pressed (100 MPa) and sintered  $1400^\circ C-2h$ . As-milled powders were evaluated by X-ray diffraction (XRD) using Rietveld method, and scanning electron microscopy (SEM). After sintering, samples were characterized by XRD, SEM, relative density, fracture toughness and 4-point flexural strength. A continuous increase in the amount of amorphous phase is observed in the powders milled up to 30h. Above this, the amorphous phase content stabilizes at about 38 vol% up to 60h. Thus, a considerable reduction in particle size is observed in SEM analyzes. In addition, the crystallite size of the  $ZrO_2$  matrix reduces from 27 nm to 10 nm, with the grinding time increasing from 1h to 60h. Fully dense samples were obtained after sintering in powder-mixture milled by 60h. Comparatively, in starting powder-mixture, high densification is obtained when samples are sintered at  $1600^\circ C-2h$ . Samples sintered at  $1400^\circ C$ , based on powders milled for 60h, presented  $KIC = 8.2 \pm 0.3 MPam^{1/2}$  and bending strength of  $880 \pm 45 MPa$ , while samples with mixture of commercial powder sintered at  $1600^\circ C-2h$ , presented  $KIC$  and bending strength of  $6.7 \pm 0.5 MPam^{1/2}$  and  $697 \pm 85 MPa$ , respectively. The improved mechanical strength observed in sintered samples with synthesized powders for 60h, by mechanical alloying, is reported with the sinterability of these powders, which allow full densification at  $1400^\circ C$ , resulting in reduction of the size of the tetragonal  $ZrO_2$  grains. Thus, a larger population of these grains is formed in the microstructure, increasing the fracture toughness and strength, by the T-M phase transformation toughening mechanism.

ID-345

**Studies of the sintering effect at different temperatures of Hydroxyapatite***A. Azzi<sup>1</sup>, L. Bahloul<sup>2</sup>, L. Alimi<sup>1</sup>, S. Guerfi<sup>1</sup>, S. Bouyag<sup>1</sup>, A. Grairia<sup>1</sup>**<sup>1</sup> Research Center in Industrial Technologie CRTI.**2- Research Laboratory of Advanced Technologies in Mechanical Production (LRTAPM), University Badji Mokhtar Annaba- ALGERIA-*

The objective of this work is the elaboration of a biomaterial Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ ), by a double decomposition chemical method ( $\text{CaCO}_3$ ,  $\text{NH}_4\text{H}_2\text{PO}_4$ ) and study of the sintering effect at different temperatures on the microstructure and morphological properties of the elaborated hydroxyapatite.

After the preparation, the powder was calcined at  $900^\circ\text{C}$ . for 90 minutes at a speed of  $10^\circ\text{C}/\text{min}$ . It was subsequently shaped into pellets and sintered at different temperatures ( $1000^\circ\text{C}$ ,  $1100^\circ\text{C}$ ,  $1200^\circ\text{C}$  and  $1300^\circ\text{C}$ ).

In our study, we have developed and characterized the composition, phase stability and density and porosity of our powder by X-ray diffraction (XRD), electron microscopy, mass loss measurement during sintering and for density and porosity were measured on a pycnometer.

The results show that the sintering temperature gives differences concerning the porosity, the density and the mass loss of elaborated material.

ID-358

**Sintering of mechanically alloyed TiC/Ti<sub>3</sub>SiC<sub>2</sub> ceramic composite***M. F. Alves<sup>1</sup>, C. Santos<sup>2</sup>, B. Freitas<sup>1</sup>, E. Ramos<sup>3</sup>, A. S. Ramos<sup>3</sup>, K. Strecker**<sup>1</sup> Universidade de São Paulo**<sup>2</sup> Universidade do Estado do Rio de Janeiro - UERJ**<sup>3</sup> Universidade Federal de Alfnas*

The present work aims to evaluate the crystalline phases and microstructure of TiC-Ti<sub>3</sub>SiC<sub>2</sub> ceramic composite, obtained by mechanical alloying and subsequent sintering from elemental Ti, C and Si powders. Ball milling was carried out in a planetary ball mill under argon (Ar) atmosphere for 1, 10, 50, 100, 200 and 300h using Ti, Si and C (molar ratio 3:1:2) as starting materials in order to prepare nanosized Ti<sub>3</sub>SiC<sub>2</sub> powders. The crystallite sizes and lattice strain of phases formed during milling and sintering were evaluated by using X-ray diffraction (XRD). The morphological characteristics and the particles size distribution were examined using scanning electron microscope (SEM). After milling, a reduction in particles size and crystallinity is observed. Furthermore, TiC is crystallized after milling for 10h. Powders milled for 200 h were compacted and subsequently sintered at 1200°C under controlled atmosphere, for 15min, 2h or 4h (5°C/min). A full densification of samples sintered at 2h and 4h is identified, with relative density near to 98%. XRD results of these sintered samples have indicated the presence of the TiC and Ti<sub>3</sub>SiC<sub>2</sub> phases. Average grain size of TiC was near to 0.7 μm. Furthermore, no grain growth was observed in sintered samples as function of isothermal holding time. The Rivetveld refinement indicates that the major TiC-cubic phase (>85vol%) presents a lattice parameter of 80.3Å after sintering at 1200°C. Despite the maintenance of Ti<sub>3</sub>SiC<sub>2</sub> cell volume, 150.5 Å<sup>3</sup>, the prolonged isotherm time leads to increase the lattice parameter “a”, from 3.15 Å to 3.20 Å, and reduce the lattice parameter “c” from “17.5 Å to 17.05 Å, indicating anisotropy in this crystalline phase as function of isothermal time. This is because Ti<sub>3</sub>SiC<sub>2</sub> is formed by layers of TiC interlaced with layers of the Si element, typical of nanolaminate materials. Thus, changes in the residual stress with the TiC matrix may occur, which must be controlled to give greater fracture toughness to the composite.

ID-362

**Sintering and characterization of ceramic based on DD3 kaolin***H. Rezzag<sup>1,2</sup>, A. Mebrek<sup>1</sup>, A. Grid<sup>1</sup>, R. Grain<sup>1</sup>, S. Bouchoucha<sup>1</sup>, S. Ladjama<sup>1</sup>, N. Touati<sup>1</sup>**<sup>1</sup> Research Center in Industrial Technologies CRT.**<sup>2</sup> Laboratory of Metallurgy and Materials Engineering (LMGM), Badji University Mokhtar Annaba- AL-GERIA*

The aim of this work was to elaborate of refractory bricks based of local kaolin from Djebel Debbagh in Algerian. The DD3 kaolin was milled for 1 h in planetary ball mill at room temperature, calcined at 1350°C for 1h, pressed into pellets, then sintered at 1250°C during 2h. The characterization of DD3 ceramics was made by X-ray fluorescence spectrometry, X-Ray diffraction and helium pycnometer. The result of the chemical composition confirmed the presence of silica (41.7%), alumina (35.8%) as principal elements and fire loss (17%). The X-ray analysis of DD3 kaolin DD3 revealed the presence of mullite as the major phase and  $\alpha$ -low cristobalite. The rate of chamotte has an influence on the change in shrinkage of the sintered samples at 1250 ° C.

ID-380

**Microstructure and mechanical properties of spark plasma sintered  $WC_6Co_xB$  ( $x = 0.2$  and  $0.5$  wt.%) ceramics**

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Tungsten carbides are one of the earliest commercial products of powder metallurgy, which are used for different applications such as the manufacture of cutting components and abrasives. Some these composites consist of tungsten carbide and metallic cobalt particles bound by sintering through the liquid phase and they can be produced by conventional chemical reactions. Previous works have indicated that alloying addition can improve their mechanical properties while the mechanical alloying and spark plasma sintering are able to homogenize and densify the ceramic compounds at low temperature, respectively. The present work aims to evaluate the microstructure and mechanical properties of spark plasma sintered  $WC_6Co$  (wt.%) ceramics doped with boron (0.2 and 0.5 wt.-%).

Metastable  $W_{50}C$  (at.%) powders were previously produced after different milling times (20, 60, 180 and 600 min) in a planetary Fritsch P-5 ball mill followed by mixing for 5 min with Co (6 wt.-%) and B (0.2 and 0.5 wt.-%) additions. Afterwards, the WC-Co-B powder mixtures were axially compacted by spark plasma sintering (SPS) at 1450°C under controlled atmosphere to obtain cylindrical bodies with height of 1-3 mm and 10 mm diameter. The starting powders and sintered products were evaluated using X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), laser diffraction particle size analysis, Vickers hardness and diametrical compression tests. The average particle sizes of the WC-Co-B powder mixtures varied between 16 and 28 micrometers following modal and bimodal distributions. SPS process from the WC-Co-B powder mixtures produced dense samples (> 96% of theoretical specific mass), which presented the WC phase as matrix beside the B-rich and  $W_2C$  precipitates. SPS samples presented Vickers hardness values between 1841 HV and 2191 HV which were more pronounced for B-richer ceramics. No effect of boron addition on the elastic module of evaluated ceramics was achieved which were close to 500 GPa. In contrary, the diametrical tensile strength of these ceramics were lower than 500 MPa.

ID-388

**Formation of compounds in the  $\text{Ag}_2\text{O}-\text{Sb}_2\text{O}_3-\text{MoO}_3$  system on heating***Y. Lupitskaya, L. Kovalenko, F. Yaroshenko**Chelyabinsk State University*

Analysis of advances in the development of novel functional materials possessing high ionic and protonic conductivity indicates that a relatively small number of compounds with tailored properties have been discovered in recent years. In this context, research concerned with the ability to modify previously synthesized substances is of particular practical importance. Among widespread materials modification techniques, it is worth noting defect formation in the crystal lattice of a host compound through doping with heterovalent impurities.

The synthesis of such materials in the form of ceramic samples makes it possible to use them as key components for the fabrication of ion-exchange and ion-conducting membranes capable of operating at elevated temperatures in fuel cells. At the same time, when heated in air the compounds in question turn out to be chemically unstable: they undergo dehydration and the reduction of pentavalent antimony ions, accompanied by the formation of phases of various compositions and structures. This paper presents a detailed study of phase formation processes in the  $\text{AgNO}_3-\text{Sb}_2\text{O}_3-\text{MoO}_3$  system during heating in air. The compositions of the solid-state reaction products have been determined using thermogravimetry and qualitative X-ray diffraction. The results demonstrate that, at a final heat treatment temperature of 1023 K, synthesis yields a range of  $\text{Ag}_{2-x}\text{Sb}_{2-x}\text{Mo}_x\text{O}_6$  compounds with the pyrochlore structure and  $0.0 < x < 2.0$ . Based on the X-ray diffraction data, we have proposed a model for the ion distribution over the crystallographic sites of space group Fd-3m: the framework of the pyrochlore structure is formed by positions 16c and 48f, which are occupied by the  $\text{Sb}^{5+}$ ,  $\text{Mo}^{6+}$ , and  $\text{O}_2$  ions at random; position 16d is partially or fully occupied by the  $\text{Ag}^+$ ; and position 8b remains vacant. It has been shown that heterovalent substitution of  $\text{Mo}^{6+}$  for  $\text{Sb}^{5+}$  in antimony oxide compounds produces defects in the pyrochlore structure and that doping of such compounds with monovalent metal ions improves their cation-conducting properties. According to our results, the highest conductivity is offered by the  $\text{AgSbMoO}_6$  phase, in which ion transport occurs through channels formed by positions 16d and 8b in the  $\langle 111 \rangle$  directions of the crystal lattice.

The reported study was funded by RFBR according to the research project No 18-33-00269.

ID-408

**Effect of  $\text{Ca}^{2+}$  addition on structural and dielectric properties of pure  $\text{BaTiO}_3$  lead free ceramic synthesized by Sol gel**A. Mahmoud<sup>1</sup>, M. Abas<sup>2</sup><sup>1</sup> Physics Department, Faculty of Science, South Valley University, Qena 83523, Egypt<sup>2</sup> Metallurgy and material science test lab (MMST), physics department, Faculty of Science, South Valley University, Qena, Egypt

Lead free  $(\text{Ba}_{1-x}\text{Ca}_x)\text{TiO}_3$  ( $0 < x < 0.1$ ) (abbreviate BCT) Perovskite were successfully synthesized by Sol gel method  $1000^\circ\text{C}$ /calcined and  $1200^\circ\text{C}$ /sintering. The effect of the addition of Sol calcium on the dielectric properties of  $\text{BaTiO}_3$  was investigated. X-ray line profile analysis has been done for the samples. Pure tetragonal single phase has been formed confirming the diffusion of Ca ions into A-site of lattice. The doping effect greatly inhibits the grain dwindle and lattice parameters. Dielectric properties and dielectric loss were enhancement by  $\text{Ca}^{2+}$  addition.

ID-415

**Transport properties and structure of melt grown  $\text{Sc}_2\text{O}_3$  and  $\text{CeO}_2$  doped  $\text{ZrO}_2$  crystals**

*F. Milovich<sup>1</sup>, M.I. Borik<sup>2</sup>, E. Lomonova<sup>2</sup>, N. Tabachkova<sup>1</sup>, D. Agarkov<sup>3</sup>, V. Bublik<sup>1</sup>, S. Bredikhin<sup>3</sup>, A. Kulebyaki<sup>2</sup>, I. Kuritsyna<sup>3</sup>, V. Myzina<sup>2</sup>, V. Osiko<sup>2</sup>*

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$\text{ZrO}_2$  based materials find general application as solid electrolytes for solid oxide fuel cells. Scandia ( $\text{ScSZ}$ ) stabilized  $\text{ZrO}_2$  base ceramics have the highest conductivity at moderate temperatures. However, a major disadvantage of these materials is the degradation of their conductivity during long-term operation due to an unstable phase composition. The materials with the highest conductivity in the  $\text{ZrO}_2$ - $(10-12)$  mol%  $\text{Sc}_2\text{O}_3$  composition range exhibit a transition from the cubic to the rhombohedral phase accompanied by a significant decrease in the conductivity. Partial replacement of  $\text{Sc}_2\text{O}_3$  for other oxides in the  $\text{ZrO}_2$ - $\text{Sc}_2\text{O}_3$  system aimed at increasing the stability of the high-conductivity cubic phase proves to be one of the most efficient solutions. From this viewpoint, one of the most attractive systems which have a high ionic conductivity at 700-900C is the  $\text{Sc}_2\text{O}_3$ - $\text{CeO}_2$ - $\text{ZrO}_2$  one. Noteworthy, the ionic conductivity of ceramics having the same chemical composition depends largely on their phase composition, microstructure, density and other parameters which in turn depend on the material synthesis technology.

In this work we report a study of  $(\text{ZrO}_2)_{2(1-x-y)}(\text{Sc}_2\text{O}_3)_x(\text{CeO}_2)_y$  solid solution crystals ( $x = 0.08-0.10$ ;  $y = 0.005-0.015$ ) grown by skull melting technique. The crystal structure of the material was studied using X-ray, TEM, Raman and impedance spectroscopy. The study showed that optically homogeneous and transparent crystals could not be grown from the melt in the experimental composition range. At an overall stabilizing oxide concentration of above 10 mol% the crystals contain the cubic and rhombohedral phases, and at an overall concentration of below 10 mol% the cubic and the tetragonal phases are present.

Ceria addition to the  $(\text{ZrO}_2)_{1-x}(\text{Sc}_2\text{O}_3)_x$  system increases the high-temperature ionic conductivity of the material, and with the ceria content being constant the conductivity of the crystals increases gradually with  $\text{Sc}_2\text{O}_3$  concentration. The lowest conductivity for the test composition range was observed in the single-phase tetragonal  $8\text{ScSZ}$ ,  $9\text{ScSZ}$  and  $8\text{Sc}_1\text{CeSZ}$  crystals. The decrease of the ceria concentration from 1.0 to 0.5 mol% leads to an increase in the high-temperature conductivity of the crystals in the entire test composition range. The highest conductivity was observed in the  $10\text{Sc}_{0.5}\text{CeSZ}$  crystals, yet they contained a lot of rhombohedral phase.

**Acknowledgements:** The work was carried out with financial support in part from the RSF (No 16-13-00056).



ID-447

**Study of  $Ti_2AlC$  nanolaminate irradiated with high-fluence ions***J. Vacik<sup>1</sup>, P. Horak<sup>1</sup>, S. Bakardjieva<sup>2</sup>, G. Ceccio<sup>1</sup>, A. Cannavo<sup>1</sup>, V. Lavrentiev**1 Nuclear Physics Institute ASCR**2 Institute of Inorganic Chemistry ASCR*

MAX phase ceramics are an important class of novel three- and two-dimensional crystalline nanocomposites with an interesting combination of metal and ceramic-like properties that have made these materials highly regarded candidates for numerous technological applications, including applications in extreme environmental conditions. The tests have shown that the MAX phases also exhibit an extraordinary radiation resistance, which could be attractive for application in nuclear industry. In this contribution, the phases of titanium aluminum carbide were inspected. The MAX phase was synthesized in thin films by low energy ion beam sputtering technique, and irradiated by high-fluence energetic Ar ions. The inspection pointed at the interesting data regarding behavior of the  $Ti_2AlC$  phase under energetic ion bombardments.

The authors acknowledge the financial support from the Grant Agency of the Czech Republic (18-21677S).

## PLENARY LECTURE

Chair: S. Laureti

**Self-assembly of carbon-based materials from nano- to macro-scale: when enemies become friends**

V. Palermo

*Institute for Organic Synthesis and Photoreactivity-ISOF, National Research Council, Italy and Chalmers University of Technology, Department of Industrial and Materials Science, Göteborg, Sweden.*

Metallic glasses are known for their outstanding mechanical strength but limited plasticity. Significant It takes more than good bricks to build a durable house. Likewise, it takes more than good molecules to build a good material: the molecular bricks should be correctly assembled in larger structures, then in mesoscopic phases, all the way up to the bulk material. In this talk, we will describe how we used covalent and non-covalent chemistry to assemble together a wide range of carbon-based building blocks such as small molecules, polymers, nanotubes and graphenes. Even if with different size and properties, they all share an extended conjugated structure, and can be functionalized and processed using covalent and supramolecular techniques,  $\pi$ - $\pi$  interactions, hydrogen bonds, etc.

In particular:

- Small poly-aromatic molecules (pyrenes, pentacenes, coronenes, polythiophenes, etc.), have a well-defined electronic bandgap and mono-dispersed nanometric size that allows their self-assembly in highly ordered stacks to give fibers, nano-crystals and uniform monolayers.
- Polymers have a much larger size, from few to hundreds of nm; they form more disordered assemblies, but their linear shape allows efficient processing, and transport of electric charges.
- Carbon nanotubes and graphene, reaching sizes up to tens of microns, have impressive optical, electronic and mechanical properties, but their processing and functionalization, as well as the control of their metallic/semiconducting properties, is still a major challenge.

We'll demonstrate that original results shall be achieved by combining together such materials with different shapes, obtaining nano-composites with novel properties and concrete applications in the fields of electronics, aerospace, energy storage or sensing.

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[2] Non-conventional processing and post-processing methods for the nanostructuring of conjugated materials for organic electronics, *Advanced Functional Materials* 21, 1279 (2011)

[3] Graphene-based nanocomposites for structural and functional applications: using 2-dimensional materials in a 3-dimensional world, *2D Materials* 2, 030205 (2015)

[4] Selective gas permeation in graphene oxide-polymer self-assembled multilayers, *ACS Applied Materials & Interfaces* 10, 11242 (2018)

[5] Application of graphene-based flexible antennas in consumer electronic devices, *Materials Today* 21, 223 (2018)

Friday 6 July morning - 9:30/11:00

Parallel Session 1  
**NANOSTRUCTURED MATERIALS XII**  
V. Palermo, Chair

**ID-418 (Invited)****Advances in two-dimensional planar spintronics***M.V. Kamalakar**Uppsala University*

Over the past one decade, graphene and other two-dimensional crystals have emerged as new testbeds for exploring fundamental physics, demonstrating great promise for new applications. In particular, for spintronics, the 2D crystals provide novel avenues for advancing towards planar spin circuits, not possible using conventional materials. For instance, graphene is a material, where spin-polarized electrons can be transported over tens of microns at room temperature, an extraordinary attribute that arises from its low spin-orbit coupling and a negligible hyperfine interaction. In my talk, first, I will introduce the field of graphene spintronics, and talk about the present state-of-the-art results in large-scale graphene, long distance spin communication capabilities, and new directions that we need to pursue to enable practical graphene spintronic applications. Followed by this, I will talk about how 2D insulators and 2D semiconductors have their own unique significance as special constituents for spintronic devices. In conclusion, I will present our latest findings, describe how the field of 2D spintronics is evolving and what new prospects it presents for future spintronics.

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ID-372

**Manufacturing technique of graphene reinforced aluminum matrix nanocomposite***H. Rudianto<sup>1</sup>, S. Scudino<sup>2</sup>, I. Dlouhy<sup>3</sup>*<sup>1</sup> *Gunadarma University*<sup>2</sup> *Leibniz Institute Dresden*<sup>3</sup> *Brno University of Technology*

Research on graphene reinforced aluminium matrix nanocomposite is growing rapidly with the expectation to increase mechanical properties of aluminum matrix. This research is mainly focused on how to disperse graphene on aluminum powder. Mechanical alloying with 10:1 ball to powder ratio was used to disperse graphene particles on aluminum powder for 10 hours under argon gas. Concentration of graphene was varied from 0.5 to 5wt%. Premix  $Al_{5.5}Zn_{2.5}Mg_{0.5}Cu$  was used as matrix. Hot compaction followed by hot extrusion was used for consolidation. It seems that agglomeration is still a problem of dispersion of carbon based materials reinforced metal matrix especially higher concentration of reinforcement particles. This agglomeration will lead to lower density of bulk aluminum. Aluminum carbide ( $Al_4C_3$ ) was found as a result reaction between graphene and aluminum during consolidation. This compound has an important role as a bridge to transport tension from matrix to graphene which gave improved mechanical properties. Raman Spectroscopy, SEM-EDS and X-Ray Diffraction (XRD) were used to characterize this nanocomposite.

ID-393

## Synthesis and characterization of graphite-encapsulated Au/Pt nanoparticles

*D. Aĝaoĝullari*

*Istanbul Technical University*

In the recent years, magnetic nanoparticles (MNPs) have been focused on with a significant interest for their possible uses in biomedical, environmental and energy applications. However, some undesired properties of MNPs such as oxidation, degradation and agglomeration limit their usage in the related applications. Encapsulating a thin protective layer on these nanoparticles and obtaining core-shell type structures are preferred as good choices to eliminate such limitations. The most utilized solution is to encapsulate magnetic nanoparticles with a multi-layer carbon shell which has excellent biocompatibility, chemical/thermal stability, electrical conductivity and strength.

Graphene-encapsulated magnetic nanoparticles have been produced via many different techniques such as carbon arc discharge, solid-state reduction, spray pyrolysis, combustion synthesis and solvothermal/hydrothermal reactions. Besides, chemical vapor deposition (CVD) method has been employed under different pressure conditions for the growth of multi-layer carbon encapsulated MNPs. CVD technique enables the control of particle size, production of pure products and repeatability of the process.

This study reports on the synthesis and, microstructural, thermal and room-temperature magnetic properties of the graphene-encapsulated Au/Pt nanoparticles prepared by a low-pressure chemical vapor deposition (LP-CVD) method. Firstly, Au(III) chloride trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ ) and Pt(IV) chloride ( $\text{PtCl}_4$ ) were impregnated into fumed silica after blending in an agate mortar, dispersing in ethanol, sonicating and drying treatments. Then, the Au/Pt/ $\text{SiO}_2$  containing precursor powders were placed into the quartz boats and into a horizontal tube furnace. The graphitization was carried out under a  $\text{CH}_4/\text{H}_2$  atmosphere at  $900^\circ\text{C}$ . The process parameters were selected as 45 min of ramping duration, 1 h of reaction duration and 80/80 ml/min of  $\text{CH}_4/\text{H}_2$  gas flow rate. Cooling atmosphere was fixed at  $\text{CH}_4/\text{H}_2$ : 80/80 ml/min. A subsequent purification step was conducted on the samples to leach out the undesired  $\text{SiO}_2$  phase. Leaching in HF solution (2 % concentration), centrifugation (at 4500 rpm for 1 h) and washing yielded pure graphene-encapsulated Au/Pt nanoparticles. The final products were characterized using X-ray diffractometer (XRD), differential scanning calorimeter (DSC), scanning electron microscope (SEM), high resolution transmission electron microscope (HR-TEM) and alternating gradient magnetometer (AGM).

ID-351

**Obtaining and thermal stability of  $\text{MnSi}_{1.75}$  intermetallic compound processed by mechanical alloying***I. Chicinas<sup>1</sup>, V. Cebotar<sup>2</sup>, T. F. Marina<sup>1</sup>, F. Popa<sup>1</sup>, B. V. Neamtu<sup>1</sup>, R. Hirian<sup>3</sup>*<sup>1</sup> *Departament of Materials Science and Engineering, Technical University of Cluj-Napoca*<sup>2</sup> *Technical University of Cluj-Napoca*<sup>3</sup> *Faculty of Physics, Babes-Bolyai University, Cluj-Napoca, Romania*

The formation of higher manganese silicide (HMS -  $\text{MnSi}_x$  chemical compound where  $x=1.72-175$ .) by mechanical alloying, starting from elemental silicon and manganese powders was studied. The milling was pursued up to 40 h to analyse the formation of HMS and stability of the compound versus milling time. After 4 hours of milling, both phases are found in material besides a significant amount of non-reacted elements. Prolonged milling, up to 10 hours, is leading to the disappearance of the silicon characteristic peaks due to the increase of the amount of HMS and  $\text{MnSi}$  phases. Also, an amorphisation of unreacted silicon is possible, leading to the disappearance of the Si Bragg peaks. After 18 h of milling, the powders showed only a mixture of HMS phase and a second phase  $\text{MnSi}$ , as indicated by X-ray diffraction studies. The elemental powders are completely reacted at this milling time. The mechanically alloyed HMS compound is nanocrystalline. A crystallite size (calculated by Williamson-Hall method) of 30 nm was obtained after 40 hours of milling. Milling for longer times, the  $\text{MnSi}$  phase amount decreased. The thermal stability of the long-milled samples was studied by differential scanning calorimetry (DSC). The DSC curves showed two thermal events: the internal stresses release recorded for temperature below 350 C° and the promotion of  $\text{MnSi}$  phase formation at temperatures around 550 C°. The particle morphology versus milling time was studied by scanning electron microscopy (SEM) and the elemental distribution maps by energy dispersive spectroscopy (EDX). The microscopy analysis showed the progressive mixing of elements. Modification of the medium particle size was studied by particles distribution measurements, and apparition of a second peak at lower dimension, associated with the biphasic character of the milled powders was recorded. The thermo-electrical properties of the consolidated powders by spark plasma sintering were studied as a part in evaluation of the potential application as thermoelectric materials of the obtained alloy.

**ID-317****Behavior analysis of some composite polymers reinforced with metallic nanoparticles**

*D. Gavrilă<sup>1</sup>, A. Caramitu<sup>2</sup>, S. Mitrea<sup>2</sup>, M. Enachescu<sup>1</sup>, V. Stoian<sup>1</sup>*

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<sup>2</sup> *ICPE-ca*

The addition of metallic nanoparticles to polymers produces changes in thermal properties, modification of dielectric properties, of intrinsic electrical conductivity, structural characteristics and polymer crystallinity. This work focuses on the effects of metallic nanopowders of Al and Fe (3, 5, and 8%) on the mentioned properties in the case of LDPE, HDPE and isotactic PP. The raw materials are mixed in a turbula in the required quantities. The mixture is extruded horizontally and then injected in the form of the samples used in the measurements. A comparative study is made in the nanocomposite materials for the electrical permittivity and the losses (frequency 50Hz) and for the electrical conductivity. The DSC method is used to highlight thermal and crystallinity changes in the temperature range of -30°C to melting temperatures. SEM measurements allowed to explain the changes in the structure of the studied nanocomposites materials.



Friday 6 July morning - 9:30/11:00

Parallel Session 2  
**METALLIC GLASSES XI**  
P. Voyles, Chair

ID-118

**Confined glass transition in amorphous/amorphous metallic nanolayers***E. Spieckermann<sup>1</sup>, M. Mühlbacher<sup>1</sup>, T. Schöberl<sup>2</sup>, C. Gammer<sup>2</sup>, C. Mitterer<sup>1</sup>, D. Soppa<sup>3</sup>, J. Eckert<sup>1</sup>*<sup>1</sup> *University of Leoben, Austria*<sup>2</sup> *Erich Schmid Institute for Materials Science, Austrian Academy of Sciences, Austria*<sup>3</sup> *Institute of Materials Science, TU Darmstadt, Germany*

Amorphous metallic coatings have recently emerged as promising thin film materials – thin film metallic glasses - due to their excellent chemical stability, good wear resistance and exceptionally high strength. Several authors have recently reported on experimental evidence that confinement may influence the ability of shear band formation in microscopic and layered metallic crystalline/amorphous samples. Shear band formation is believed to be related to highly localized structural or dynamic inhomogeneity. Little data exists, however, on the influence of confinement on the glass transition in bulk metallic glasses. In order to study the influence of a confined glassy structure, we prepared purely amorphous/amorphous layered thin films of CuHf and CuZr with layer thicknesses ranging from several nanometers to 1  $\mu\text{m}$  by unbalanced dc magnetron co-sputtering from elemental targets. Systematic thermal analysis has been performed using conventional and modulated scanning calorimetry in order to study the specific glass transitions of the constituting components as a function of the layer thickness. The results are backed with experiments characterizing the structural properties by transmission electron microscopy and X-ray diffraction. Hardness and elastic properties were studied using nanoindentation. Theoretical assessment by molecular dynamics simulations indicate a significant mobility in the interface regions and confirm a shift of the glass transition temperature.

## ID-120

**Enhancing the tensile ductility of bulk metallic glasses by designing structural heterogeneities**

*S. Scudino<sup>1</sup>, J. Bian<sup>2</sup>, H.S. Shahabi<sup>3</sup>, D. Sopa<sup>4</sup>, J. Sort<sup>5</sup>, J. Eckert<sup>6</sup>, G. Liu<sup>2</sup>*

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A precondition to exploit the full potential of the structural heterogeneities for mitigating the room-temperature brittleness of bulk metallic glasses (BMGs) is to understand their influence on the shear banding mechanism. This task necessitates the ability to generate heterogeneous microstructures with designed morphology. Here, by using experimental and computational methods, we examine the interaction between shear bands and the linear, periodic heterogeneities generated by mechanical imprinting. The imprinted BMG is elastically heterogeneous and mechanically anisotropic: the Young's modulus varies periodically and the strength and ductility under tension increase with changing the orientation of the heterogeneities. This behavior takes place through shear band branching and their gradual rotation. Molecular dynamics and finite element simulations suggest that these phenomena initiate at the interface between the heterogeneities, where the shear banding mechanism characteristic of homogeneous glasses is perturbed.

ID-239

**Structural features of binary amorphous Zr-TM and Al-TM alloys as an aid towards a better understanding of multinary bulk metallic glasses***M. Stiehler, M. Jolly, K. Georgarakis**School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield MK43 0AL, UK*

Bulk metallic glasses containing Zr and Al are a promising class of materials for future applications. It is known that the addition of Al to binary Zr-TM metallic glasses leads to an improvement in their glass-forming ability (GFA). A higher number of components, however, causes a multitude of possible influencing factors making it difficult to discern the mechanisms underlying the stabilization of the amorphous phase in these multinary alloys.

In this work, we therefore report on structural features of binary amorphous Zr-TM and Al-TM alloys as subsets of the Zr-TM-Al alloys. Especially the structure of the Al-TM systems is discussed in terms of Hume-Rothery-like interactions between the global subsystems of the electrons on the one hand and the static structure on the other hand. The electronic system is strongly influenced by hybridization effects between the Al-sp- and the TM-d-states close to the Fermi energy. Although the GFA of these binary systems is typically limited, they can be seen as model systems to study fundamental structure forming processes also being effective in the multinary Zr-based bulk glassy alloys offering useful insights for a better understanding of bulk glass formation.

ID-336

**Highly oriented ferromagnetic polymers based on Co-rich amorphous microwires***V. Bautin<sup>1</sup>, A. Seferyan<sup>1</sup>, E. Kostitsyna<sup>1</sup>, N. Perov<sup>2</sup>, N. Usov<sup>1</sup>*<sup>1</sup> *National University of Science and Technology «MISIS»*<sup>2</sup> *Faculty of Physics, Lomonosov Moscow State University*

In this paper highly oriented magneto- polymer composites have been synthesized based on  $\text{Co}_{67}\text{Fe}_4\text{Ni}_2\text{Mo}_2\text{B}_{11}\text{Si}_{14}$  amorphous microwires in a glass shell [1] with a metal nucleus diameter  $d = 15.66 \mu\text{m}$ , total diameter  $D = 30.44 \mu\text{m}$  and length  $L \sim 5 - 6 \text{ mm}$ . The saturation magnetization of the ferromagnetic core of the microwires is  $M_s = 500 \text{ emu/cm}^3$ . The microwire segments were oriented in the magnesium alloy form and were poured with a liquid polymer whose composition was a mixture of methyl methacrylate methacrylic acid and methacrylate copolymers in a ratio of 37/63% by mass. The samples were polymerized in a hyperbaric pressure chamber for 15 minutes at a pressure of 3 bar. The volume fraction of the magnetic material in the polymer matrix was 0.04. The saturation field of the polymer along the axis of the microwire orientation is approximately 10 Oe, but if the sample is magnetized in the direction perpendicular to the axis of preferable wire orientation, the saturation field of the composite is greater than 4000 Oe. The highly-oriented magneto-polymer composites obtained possess high specific electric resistance, chemical stability, mechanical strength and have high average saturation magnetization  $M_s = 20 \text{ emu/cm}^3$ . The polymer samples can be cut into pieces of arbitrary size and shape. This opens up wide possibilities for their use, in particular, in biomedicine.

This work was supported by the Ministry of Education and Science of the Russian Federation in the framework of Increase Competitiveness Program of NUST «MISIS», contract № K2-2017-008.

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ID-287

**Size-dependent transition in the failure mode of brittle metallic glass***B. Qu<sup>1</sup>, D. Tönnies<sup>1</sup>, Z. Liu<sup>2</sup>, Z. Zhang<sup>2</sup>, C. Volkert<sup>1</sup>*<sup>1</sup> *Institute of Materials Physics, University of Göttingen*<sup>2</sup> *Institute of Metal Research, Chinese Academy of Sciences*

On reducing sample size into the sub-micrometer scale, the mechanical response of metallic glasses (MGs) are often changed dramatically. For instance, obvious tensile ductility and necking can be observed in nano-scale MGs, while they are rarely seen in bulk samples. Here we present our recent studies of the size effect on the deformation and failure behaviour of two kinds of brittle MGs, including an ultrahigh-strength Co-based MG and a fully annealed MG. A failure mode transition is observed in both glasses on decreasing the sample size. The bulk samples failed by fragmentation under compression and normal fracture under tension, similar to other brittle MGs, while the micrometer and sub-micrometer scaled specimens demonstrated shear banding, typical of ductile MGs. 3D X-ray tomography observations on a bulk compressive sample deformed to just before fragmentation confirmed that the fracture of bulk samples proceeds by splitting cleavage cracking rather than shear banding. The inherent mechanism of this size-dependent failure mode transition, as well as the application of these results to further understand the mechanical properties of MGs, will be discussed.

**ID-241****A study of structural evolution of a Pd based metallic glass using fluctuation electron microscopy**

*L. Tian, D. Tönnies, V. Roddatis, C. Volkert*

*University of Göttingen*

Structural characterization of metallic glasses is of great importance for understanding their properties. In recent years, efforts have been made in developing new methods to address this issue. Fluctuation Electron Microscopy (FEM) is a transmission electron microscopy based method which is effective in characterizing medium range order (MRO) of an amorphous system. By taking scanning nanobeam electron diffraction data, statistical analysis of the coherent scattering from nanoscopic volumes can be obtained. Using this method, we characterize the structure of a  $\text{Pd}_{77.5}\text{Cu}_{6.0}\text{Si}_{16.5}$  MG in different structural states induced by thermal annealing, cooling to cryogenic temperatures, and mechanical deformation. Clear changes in MRO have been found in samples which experienced different thermal history. By applying this method to an in-situ tensile sample, a surprising tendency for formation of nanocrystals is revealed.

Friday 6 July morning - 9:30/10:45

Parallel Session 3  
**MECHANICAL PROPERTIES III**  
Z. Wang, Chair



**ID-37****Elastic and Anelastic behavior of small dimensioned Aluminum**

*E. Campari*<sup>1</sup>, *E. Bonetti*<sup>1</sup>, *S. Amadori*<sup>1</sup>, *R. Berti*<sup>1</sup>, *R. Montanari*<sup>2</sup>

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<sup>2</sup> *Università degli Studi di Roma TorVergata*

Decreasing the dimension of a material down to the submicrometric regime may have relevant effects, for instance on its mechanical, optical and magnetic properties. In the case of Aluminum clear differences exist between single or large grained samples and samples with submicrometric structure. In the specific case of anelasticity, recent results demonstrate that grain size and/or materials thickness modify both temperature and time dependence of anelastic relaxation processes with respect to those observed in bulk samples. In the present research, results are presented regarding anelasticity on 5N pure Aluminum in the shape of thin films, deposited on silica substrates with thickness down to 0,1  $\mu\text{m}$  and free standing sheets obtained by cold rolling down to 6  $\mu\text{m}$ . Dynamic elastic moduli and internal friction have been measured with a vibrating reed analyser under vacuum in the frequency range 50-1000 Hz in the temperature range 250-750 K. The thermally activated anelastic relaxation processes, observed on films, are strongly dependent on film thickness below a critical value and also on the presence or absence of the rigid substrate; both the activation energy and the relaxation strength are affected by film thickness.

These results, together with those observed on bulk samples, are indicative of specific dislocation and grain boundary dynamics, constrained by critical values of the ratio of film thickness to grain size.

ID-205

**Mechanical properties of a hot rolled and annealed medium Mn automotive steel**

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In the last years, a multitude of bulk metallic glasses (BMGs) with interesting properties were developed. Additionally, to classical single-phase BMGs, also bulk metallic glass composites (BMGCs) are produced to adjust the properties by introducing an additional crystalline or amorphous phase. In this work, high pressure torsion (HPT) was used to produce BMGs and BMGCs starting from powders. The powders were mixed (amorphous and crystalline) by hand and subsequently compressed and welded together via a HPT tool until fully dense disks were achieved. A great advantage is the flexibility of the chosen phases and their ratio. Amorphous/amorphous and amorphous/crystalline BMGCs can be produced easily and the size scales of the composites (from nanometer to micrometer) can be varied by changing the applied strain during the HPT-process. The mechanical properties of BMGCs were characterized by means of hardness measurements, compression tests, tensile tests, and nanoindentation. In-situ micro-pillar compression tests were conducted to investigate the influence of the second phase revealing a strong dependence of its type, fraction, and orientation. Thinner lamellae of the crystalline phase and partial mixing increases the strength of the material, but thicker lamellae and a favorable orientation increases the ductility and stopping of shear bands can be observed. Activation volume and energy of shear bands were determined by nanoindentation jump tests leading to the conclusion that the initiation of shearing is mainly governed by the homologous temperature of the different compositions, while adding a second phase may play a role for the propagation of shear bands.

**ID-156****A novel numerical approach to simulate 3D printing material**

*S. Abid<sup>1,2</sup>, T. Hassine<sup>1</sup>, H. Nouri, M-F Lacrampe<sup>2</sup>, H. Daly<sup>1</sup>*

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Parts fabricated by the FDM technology, are characterized by a specific macrostructure. Layers are called together without material fusion as the layers are deposited with alternatively orientations. To realize the numerical simulation, a three dimensional solid model are generated under ABAQUS to have similar macrostructure of the parts which printed. This model was prepared at different orientation and direction. This study focuses on a method for simulation to have the elastic property of the printed ABS polymer. According to our experimental results the optimal printing angle is at  $+45^{\circ}/-45^{\circ}$ . This sequence of filaments shows the best behaviour in elastic part.

ID-406

**In situ micro-cantilever tests to study fracture behavior of magnesium reinforced with carbon nanotubes by an alternative technique***C. Merino<sup>1</sup>, J. Ramírez<sup>2</sup>, J. Meza<sup>3</sup>, J. Rudas<sup>4</sup>**1 Institución Universitaria Pascual Bravo**2 Centro de Investigación en Materiales Avanzados (CIMAV)**3 Universidad Nacional de Colombia - Medellín**4 Institución Universitaria Pascual Bravo, Grupo GIEN*

During three decades, several research centers have tried understanding the carbonaceous behavior in carbon nanotubes, and an outstanding potential of this kind of materials for structural applications as a reinforcement in composites materials with polymeric [1], ceramic [2] and metallic matrices (MMCs) [3-4]. The metal matrix composites (MMCs) have been used in several applications in the aerospace and aeronautic industry. Carbon nanotubes (CNTs), discovered in 1991 by Iijima [5], have come to the scene as a reinforcing material, mainly because of their very good mechanical properties [6]. However, their dispersion and alignment are still paramount variables that are not easily controlled by almost any manufacture method [7-8]. Recently a promissory technique, the sandwich technique, for the manufacture of metallic matrix composite materials has been proposed. This technique produces a material comprised of a metallic matrix and a banded structured-layers of MWCNTs and allows obtaining an increase in stiffness, strength and fracture toughness of this type of materials. This work uses micro-cantilever bending experiments conducted inside a Transmission electron microscope (TEM) (in-situ experiments) and high-resolution transmission electron microscopy (HRTEM). The results show different strengthening mechanisms like dislocation stacking and dislocation nucleation at the interface between carbon nanotubes and the metallic matrix, grain size reduction close to the interface and some interaction between carbon nanotubes and aluminum and magnesium; finally, the crack path was identified for the composites studied after in situ test. The results suggest different mechanism during the cracking growth such as ductile and fragile failure and were verified by TEM and HRTEM microscopy techniques. Likewise, the fracture behavior by the grain size and reinforcement effect was analyzed and correlated.

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## ID-297

**Effect of direct addition of Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> on mechanical behaviour of austenitic ODS SS316L steels**

*K. Gothandapani, B.S. Murty*

*IIT Madras*

Advancement of nuclear system requires different cladding and structural materials. Fuel pins inside the cladding tube undergo intense irradiation at high temperatures. Life period of fuel pins largely depends on the temperature and irradiation to which they are exposed. Due to high breeding ratio of the fuels used in the fuel pins, the materials undergo void swelling, irradiation creep and irradiation embrittlement. Hence, the cladding tube requires high swelling resistance and creep strength for increased life span. The first-generation material, austenitic stainless steel can withstand only up to 50 displacements per atom (dpa). For the doses above 50dpa, ferritic/martensitic steels are used. Ferritic/martensitic steels exhibit high swelling resistance than austenitic steels but their poor thermal creep strength at operating temperatures limits their usage. To overcome this problem, new emerging materials, namely, oxide dispersion strengthened (ODS) steels have been developed.

These ODS steels are processed mainly through powder metallurgy route. The properties of ODS steels primarily depends on microstructure, particularly the size and number density of clusters formed in these steels. Commonly used oxides for ODS steels are Y<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub> and TaO<sub>2</sub>. The nature, type, amount of oxides and other alloying elements also affect the properties of these steels. In presence of Ti, Y<sub>2</sub>O<sub>3</sub> is known to react with Ti to form Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub> during consolidation. Similarly, we can substitute heavy atoms such as Zr and Hf to form Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> compounds. These finely dispersed, nanometre sized particles restrict dislocation motion, thereby improving mechanical properties, while simultaneously generating a large number of particle-matrix interfaces, which act as a sink for radiation induced defects. In this study, the effect of dispersoids in austenitic steel (SS316L) have been studied in two ways. First, by direct synthesis of Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> through mechanically activated synthesis. Second, adding Y<sub>2</sub>O<sub>3</sub>, Ti, Zr and Hf to form in-situ oxides. The milled powders are consolidated by spark plasma sintering. The microstructure, hardness and compressive behaviour of the sintered pellets were characterized using different techniques. The high temperature mechanical properties of ODS steel with direct addition of Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub> are compared with those within-situ formed Y<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, Y<sub>2</sub>Zr<sub>2</sub>O<sub>7</sub> and Y<sub>2</sub>Hf<sub>2</sub>O<sub>7</sub>.

Friday 6 July morning - 9:30/11:00

Parallel Session 4  
**PHASE TRASFORMATION III**  
M. Kaufmann, Chair

**ID-144****Existence of recrystallized and seaweed structures in rapidly solidified Ni<sub>3</sub>Ge Intermetallic**

*N. Haque, R.F. Cochrane, A.M. Mullis*

*University of Leeds, UK*

The congruently melting, single phase intermetallic  $\beta$ -Ni<sub>3</sub>Ge has been subject to rapid solidification via drop-tube processing wherein powders, with diameters between 75 to  $\leq 38 \mu\text{m}$ , are produced. At low cooling rates (75 – 53  $\mu\text{m}$  diameter particles, 23000 – 42000 K/s) the dominant solidification morphology, revealed after etching, is that of isolated recrystallized structure. At higher cooling rates (53 – 38  $\mu\text{m}$  diameter particles, 42000 - 54000 K/s) the dominant solidification morphologies are the mix of recrystallized and dendritic seaweed structure, along with a featureless matrix. However, at the highest cooling rates ( $\leq 38 \mu\text{m}$  diameter particles,  $> 54000$  K/s) the dominant solidification morphologies are the isolated dendritic seaweed, again imbedded within a featureless matrix. Selected area diffraction analysis in the TEM reveals the recrystallized and the featureless matrix of all samples are the ordered variant of the Ni<sub>3</sub>Ge, while dendritic seaweed is the disordered variant of the same compound. It is also observed that the recrystallized structure completely transformed in to dendritic seaweed at highest temperature. Microvicker hardness test shows that mechanical properties improves with decreasing the particle size from the 75 to  $\leq 38 \mu\text{m}$  as a consequence of increasing cooling rate.

ID-262

**Study of colour and mechanical property by transition of  $Mg_2Si$  to Si phase distribution and ratio of Al-based blue colour alloy***S. Mun, K-B Kim, S-Y Choi, H-J Park, S-H Hong, Y-S Kim, S-J Kwon, S-W Park**Sejong University*

Al-based alloys is used in exterior materials with colouring are applied colour mounting technology only to the surface via surface treatment. When external physical pressure is generated, coated colour in surface is deleted and the colour of the Al-based alloy itself is appeared to the outside. In addition, colour coating through surface treatment can be applied only to single phase Al-type alloys, so it has great difficulty to simultaneously apply light weight/high strength properties and colour coating technology. Also existing metal colour like Cu- and Au-nonferrous metals, colour transition and mechanical properties control techniques have already reached technical limits. In the future, in order to apply high value-added sensibility fused material-design industry, beyond colour realization range of existing technology. Development of high value-added colour alloy/material technology that can realization whole colours in the visible light region is required. In order to overcome these disadvantages, we can suggest a method of using a colour intermetallic compound, which has a unique colour with its own atomic structure by taking a pseudo-gap. In this study, make use of the control alloy design technique above, selective precipitation of intermetallic compounds that realize blue colour/Al in matrix has unique colour of alloy itself through crystallization, excellent colour durability and a light weight/high strength property at the same time.



**ID-329****Effect of nitrogen on the mechanical properties of FCC high entropy alloys***J-S Lee<sup>1</sup>, K-N Yoon<sup>1</sup>, H-S Oh<sup>2</sup>, S-J Kim<sup>1</sup>, E-S Park<sup>1</sup>**<sup>1</sup>Seoul National University**<sup>2</sup>Research Institute of Advanced Materials, Department of Materials Science and Engineering, Seoul National University*

Hydrogen, oxygen, carbon, and nitrogen occupy interstitial sites in solid solution alloys playing an important role in affecting the lattice parameter, stacking fault energy (SFE), phase stability, and microstructure. Among several known deformation behaviors, twinning-induced plasticity (TWIP) and transformation-induced plasticity (TRIP) effects had been shown to have a direct correlation with the stacking fault energy of a material. The transition of predominating effect shifts from TWIP to TRIP as the SFE is lowered. Previous studies have shown that in the case of austenitic steels, the effect of nitrogen on the SFE depends on the alloyed concentration of nitrogen. Meanwhile, high entropy alloys (HEAs) were recently developed, exhibiting better mechanical properties from extremely low to high temperature ranges. However, in the case of HEAs, no studies on the SFE upon nitrogen addition have been reported to our knowledge. Therefore, this work investigates the effects of nitrogen addition on the SFE via observation of mechanical properties and deformation behavior in HEAs by employing tensile test, electron microscopy and characterization techniques in the alloys with varying nitrogen concentration. As a result, we report an improvement in strength and ductility along with retained TRIP effect. This investigation contributes to the unexplored area of HEA research to better understand and fine-tune the mechanical properties for expanding the applicability of the newly developed alloys.

ID-339

**Effect of cooling rate on the microstructure and mechanical property of commercial grey iron rapidly cooled in Nitrogen and Helium***O. Oloyede, N. Haque, R. Cochrane, A. Mullis**University of Leeds, UK*

To understand the interdependence of microstructure and property of an alloy on its production processing route is essential in predicting its eventual performance in service. Although the conventional solidification process during metal casting process can be predicted but further investigation is required to explain evolved phase formation when such is rapidly solidified using containerless process and different cooling media. Hence, over the years, rapid solidification of metals and alloys have evolved from mere laboratory-scale research experiments to full commercial-scale manufacturing operations. In this study, emphasis is actually on show-casing the re-engineering effect of cooling rate on as-cast material via containerless solidification processing on its morphology, microstructure and mechanical properties of an important commercial engineering material BS1452 grade 250 grey iron.

Droplets were produced in N<sub>2</sub> as cooling medium using a 6.5 m height drop-tube located in Institute for Materials Research (IMR), University of Leeds, UK. The rapidly solidified particles were collected and sieved into 8 different sizes ranging from ~53 to ~850 µm diameters with corresponding cooling rate of ~900 to ~78,000 Ks<sup>-1</sup>. The particles phase and microstructure changes were examined using optical, SEM, XRD and TEM techniques to ascertain the phase transformation noticed. Meanwhile, the change in mechanical property was measured in terms of microindentation using Vicker hardness tester and as the cooling rate increases the undercooling increase as well which was confirmed with TEM pattern indexing. It was observed that there was steady phase transformation from the ferritic phase of the as-cast to a mixture of retained austenite phase with either of the two extreme in the medium size droplets and eventual increasing martensitic phase in the droplets with increasing cooling rate i.e. decreasing particle size; which resulted in near doubling of the microhardness of the ~53 µm droplets as compared to that of the control sample i.e. the as-cast. Hence, powder metallurgy practice of various commercial alloys is on increase to preserve inherent microstructure and property of the alloys as desired for service.

ID-476

**Alpha phase precipitation in Ti-Mo alloys with Sn addition during aging heat treatment***M.G. de Mello, R. Caram**University of Campinas*

Application of metastable beta Ti alloys in several fields, from medicine to aerospace industries, is becoming ever more relevant, which is due to their unique features, like enhanced biocompatibility, improved corrosion resistance and unique mechanical behavior. While Mo is a well-known beta stabilizing alloying element in Ti alloys, Sn is known to be an effective suppressor of omega phase precipitation. An interesting Ti alloy with possible application in load bearing devices for biomedical implants is related to the  $Ti_{13}Mo_6Sn$  alloy (wt. %). In Ti alloys, specific processing conditions can lead to alpha phase precipitation into beta phase matrix, which results in high mechanical strength combined with reasonable ductility. This work aims to examine the effect of Sn addition to Ti-Mo alloys and verify microstructure evolution during aging of solution heat treated samples. Samples were arc melted and plastic deformed. Following, they were solution heat treated at temperatures in the beta phase field, water quenched and then, processed at different conditions. Differential thermal analysis was applied to identify phase transformation temperatures. Results obtained indicate that Sn addition allows suppression of omega phase precipitation, which affect alpha phase precipitation and hence, mechanical behavior. Also, aged samples showed very refined alpha phase precipitates into beta phase matrix.

ID-446

**A kinetics-based model for prediction of final phases in equiatomic High Entropy Alloys***C. Chattopadhyay, A. Prasad, B.S. Murty*

A very simple and completely predictive model has been designed to predict the final phases that will form in an equiatomic high entropy alloy (HEA). The model has been designed in a way to predict whether an equiatomic HEA will form a single phase BCC, FCC, HCP or a mixture of two or more with or without intermetallic compound phase (IM). The model takes care of the prediction of amorphous phase for an equiatomic HEA too. A very important kinetic parameter for any phase transformation is viscosity of constituting elements. Thus, the viscosity of alloy has been modelled principally as a function of viscosities of constituting elements, the crystal structure of the probable hypothetical final crystalline phase, the packing factor of the crystal system and atomic size variation in elements. TTT diagram of a crystalline phase or IM phase has been constructed with the help of the modelled viscosity of an alloy. Hence, the TTT diagram has been developed solely depending on elemental properties and an alloy has been considered to form all possible lower order split ups to form crystalline solid solution phase or IM phase in binary to the order of the alloy. The hierarchy of the TTT diagram have been studied and from the hierarchy, the final phase or combination of phases have been predicted. All equiatomic HEAs studied so far have been investigated with the present model and the model have been found to be excellently efficient in predicting the final phase or combination of phases. CoCrCuFeNi, CoCrFeMnNi, AlCoCrFeNi AlCuMgMnZn, ZrTiNiCuBe are few examples of the alloys studied. Moreover, the model can explain the various outcomes in different cooling rates in many HEAs like AlCoCrFeNi. AlCoCrFeNi and CoCrFeMnNi have been experimentally studied in melt spinning for their amorphisation behaviours. The results prove the prediction of the model to be correct.

**Friday 6 July morning - 11:30/12:45**

Parallel Session 1  
**NANOSTRUCTURED MATERIALS XIII**  
D. Mirabile Gattia, Chair

ID-441

**Processing of high strength Al alloy composites reinforced with functionalized multi-walled carbon nanotubes (MWCNT)***E.M. Mazzer<sup>1</sup>, M.C.C. Souza<sup>2</sup>, M.D.V. Felisberto<sup>3</sup>, I. Martins<sup>3</sup>, T.H.R. da Cunha<sup>3</sup>*<sup>1</sup> *Department of Metallurgical and Materials Engineering, Universidade Federal de Minas Gerais*<sup>2</sup> *Microscopy Center, Federal University of Minas Gerais,*<sup>3</sup> *Center of Technology in Nanomaterials- CTNano, Technological Park of Belo Horizonte- BHTec,*

Aluminium alloys of the 7000 series are widely used in aerospace and automotive industry due to its high strength to density ratio. However, the survey for stiffer materials with higher strength and lower density has attracted attention to Al metal matrix composites. Due to its ultrahigh elastic modulus (~1 TPa), ultrahigh strength (~100 GPa) and large aspect ratio (up to 1000), carbon nanotubes are considered a promising reinforcements for Al-matrix composites. Generally, classic powder metallurgy techniques are used to consolidate the composites, such as high energy ball milling and pressing. Then the samples are pressed and sintered in many different approaches. The main issue of this route is the heterogeneous distribution of the CNT due to the strong van der Waals interactions between the tubes, which impairs the strengthening potential of the reinforcement. Based on the previous works in the literature, many consolidation attempts have been developed to solve this issue on pure aluminum. However, just a few works focus on high strength Al alloys, such as the Al-Zn-Mg-Cu (7xxx series). The present work aims the processing and characterization of an Al AA7050 matrix composite reinforced with multiwalled carbon nanotubes (MWCNTs) in a new route. MWCNTs were produced by chemical vapor deposition (CVD), functionalized using sulfuric and nitric acid and dispersed in a mixture of ethylene glycol monobutyl ether and water (50/50%) using a three-roller mill. AA7050 alloy powders were produced by N<sub>2</sub> gas atomization and then sieved in a size range between 45 and 80 m. The MWCNT suspension and the alloy powders were mixed together in different proportions in a bath sonicator for 20 min. After the mixture processing, the CNT suspension/Al alloy particles were put in a rotary evaporator for gentle removal of the solvents from samples by evaporation. The powders were cold pressed in a mold with 7,5 mm diameter at around 3GPa and sintered at 500°C for 1 hour in an argon flow furnace in order to get the final composite. The microstructure of the powders/CNT and the final composites were characterized by SEM, TEM, Raman spectroscopy and X-ray diffraction. Mechanical properties were evaluated by microhardness. A homogeneous distribution of the MWCNTs was found in the matrix, which can be linked to the improvement found in the mechanical properties. It can be said that a new route had been performed for metallic composites reinforced by CNT.

ID-442

**Production and characterization of VO<sub>x</sub> nanostructured thin films***A. D'Elia<sup>1</sup>, M. Coreno<sup>2</sup>, C. Cepek<sup>3</sup>, C. Spezzani<sup>4</sup>, M. de Simone<sup>3</sup>, A. Marcelli<sup>5</sup>, P. Piseri<sup>6</sup>*<sup>1</sup> University of Trieste/IOM-CNR<sup>2</sup> ISM-CNR, Istituto di Struttura della Materia<sup>3</sup> IOM-CNR, Istituto Officina dei Materiali<sup>4</sup> Elettra Synchrotron Light Source<sup>5</sup> LNF-INFN, 3. ISM-CNR, Istituto di Struttura della Materia, 6. RICMASS, Rome International Center for Materials Science Superstripes<sup>6</sup> CIMaNa, Dipartimento di Fisica, Università di Milano

Gas phase synthesis of nanoparticles is scientifically relevant for technological applications, since this production method is the most eligible candidate to integrate nanostructured (NS) materials into micro-electronic devices [1]. Recently, our interest has been devoted to the synthesis of vanadium oxides with a metal oxidation state ranging between 4 and 5. These oxides are fascinating and widely studied. As an example, because of their planar structure, both V<sub>2</sub>O<sub>5</sub> and V<sub>6</sub>O<sub>13</sub> have been deeply investigated for possible applications as Li ion battery cathode materials [2,3]. VO<sub>2</sub> is instead investigated because it undergoes a reversible metal-insulator-transition (MIT) near room temperature. This material is of a great interest for the realization of switching devices, memory materials and energy storage [4,5]. Many foreseen applications are enhanced going to nanoscale, because of quantum size effects. Indeed, at low dimensionality the electronic and structural properties of NS materials may strongly differ from the bulk analogue. Among the different gas phase methods, the Supersonic-cluster-beam-deposition (SCBD) by means of a Pulsed Microplasma Cluster Source (PMCS) [6] is among the most promising approach for industrial applications [7]. Its strength relies on the intense and stable nanoparticle beam production and on the versatility in materials it can produce. SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and PdO<sub>x</sub>, is a small list of the oxides that can be obtained by SCBD/PMCS [1]. We report preliminary results from our systematic production of vanadium oxides NS thin films characterized via in-situ X-Ray and Ultra-Violet Photoelectron Spectroscopy and ex-situ Raman and X-ray absorption spectroscopy. Using these techniques, we can determine the chemical state of the NS films, probe the presence of quantum size effects and evaluate how they affect electronic and structural properties [8]. Data will be compared with the results obtained on strained VO<sub>2</sub> thin films [9].

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## ID-75

**Effect of Aluminium content on oxidation behavior of arc melted  $\text{Al}_x\text{CoCrFeNi}$  ( $x=0,0.3,0.6,1$  mole) high entropy alloys exposed at  $1150^\circ\text{C}$  and comparison with nanocrystalline  $\text{Al}_{0.6}\text{CoCrFeNi}$  high entropy alloy**

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High entropy alloys (HEA) containing Al and Cr have been observed to manifest impressive dry air oxidation resistance. But the testing temperature attempted in the previous works has been restricted up to  $1050^\circ\text{C}$ . In the present work  $\text{Al}_x\text{CoCrFeNi}$  HEAs ( $x=0,0.3,0.6,1$  mole) synthesized by arc melting route have been subjected to rigorous dry air oxidation test up to  $1150^\circ\text{C}$ . The as cast HEAs with  $x=0$  and  $x=0.3$  show single phase FCC structure whereas those with  $x=0.6$  and  $x=1$  shows dual phase FCC+BCC structure and dual phase B2+BCC structure respectively. Increase in Al content increases the Al, Ni rich BCC phase fraction. Subjected to oxidation at  $1150^\circ\text{C}$  for 24h,  $\text{CoCrFeNi}$  ( $x=0$ ) developed a continuous  $\text{Cr}_2\text{O}_3$  layer, while for  $\text{Al}_{0.3}\text{CoCrFeNi}$ , a  $\text{Cr}_2\text{O}_3$  surface layer and internal discontinuous  $\text{Al}_2\text{O}_3$  was observed. Under same testing condition  $\text{Al}_{0.6}\text{CoCrFeNi}$  and  $\text{AlCoCrFeNi}$  HEAs exhibited a single layer of protective, adherent, tenacious and continuous  $\text{Al}_2\text{O}_3$ .  $\text{Al}_{0.6}\text{CoCrFeNi}$  was also synthesized via mechanical alloying and consolidated by spark plasma sintering to produce nanocrystalline HEA having FCC+BCC structure. When the nanocrystalline  $\text{Al}_{0.6}\text{CoCrFeNi}$  HEA was subjected to similar oxidation parameters it has formed a protective continuous  $\text{Al}_2\text{O}_3$  oxide layer relatively sooner than microcrystalline  $\text{Al}_{0.6}\text{CoCrFeNi}$  synthesized by arc melting. This can be attributed to the large grain boundary area available in the nanocrystalline HEA which acts as pathways and facilitates easier grain boundary diffusion and hence quicker formation of the protective oxide layer. The oxidation resistance of  $\text{Al}_{0.6}\text{CoCrFeNi}$  and  $\text{AlCoCrFeNi}$  HEAs exceeds manifold than that of  $\text{CoCrFeNi}$  and  $\text{Al}_{0.3}\text{CoCrFeNi}$  as well as is far superior to that of Inconel 718 and Inconel 600 superalloys in terms of oxide layer thickness, adherence, stability and protective nature. This is due to their higher Al content which remains dissolved in the multicomponent BCC phase owing to configurational entropy stabilization. The oxidation resistance is also observed to increase with the corresponding increase of the multicomponent BCC phase fraction which acts as the reservoir of Aluminum.

## ID-92

**Development of P-free Fe-Si-B-Cu soft magnetic nanocrystalline alloys with high Cu concentrations**

*Y. Li, Xingjie JiaNone, X. RenNone, W. Zhang, G. XieNone*

*Dalian University of Technology*

The demand for energy saving and device miniaturization drives the development of soft magnetic materials to the direction of high saturation magnetic flux density ( $B_s$ ), high permeability, and low core loss. Soft magnetic Fe-Si-B-P-Cu nanocrystalline alloys with high  $B_s$  of  $\sim 1.85$  T and low core loss seem to be promising magnetic core materials [1]. However, the alloys contain phosphorus and have to be annealed under a high heating rate to obtain a fine nanostructure [2], which brings great challenges for industrial production. In this work, with aim to develop soft magnetic Fe-based nanocrystalline alloys with high  $B_s$  and good manufacturability, we designed a simple Fe-Si-B-Cu alloy system containing high Fe contents of  $> 80$  at.% and Cu contents of  $\geq 1.3$  at.%, and investigated the microstructure and magnetic properties of the alloys. It was found that the nanocrystalline alloys with high  $B_s$  of  $\sim 1.77$  T and low coercivity of  $\sim 7.1$  A/m can be obtained by annealing the melt-spun Fe-Si-B-Cu alloys containing Cu contents of 1.7-2.0 at.%. The high Cu concentration facilitates the formation of high-number-density  $\alpha$ -Fe nuclei pre-existing in the amorphous matrix, which inhibits the excessive growth of the  $\alpha$ -Fe grains by their competitive growth even during the low-heating-rate annealing, resulting in a fine nanostructure and excellent soft magnetic properties. In addition, the effect of Nb addition on the structure and magnetic properties of the Fe-Si-B-Cu nanocrystalline alloys was investigated as well.

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ID-115

**Effects of Mg content and annealing temperature on electrical and optical properties of ITO/AgMg films***H.K. Lin, Y.J. Huang**National Pingtung University of Science and Technology*

AgMg (AM) and ITO/AgMg (IAM) films with Mg contents ranging from 25~60 at% are deposited on glass substrates and are then annealed at different temperatures. The electrical and optical properties of the as-deposited and annealed samples are investigated. It is apparent that the transmittance of the AM film decreases, while the sheet resistance increases following increasing the Mg content. For a Mg content of 33 at%, the IAM sample improves the resistance from  $22.9 \Omega/\square$  (AM) to  $21.6 \Omega/\square$  (IAM) and the transmittance increases from 57.1% (AM) to 76.4% (IAM) due to the bi-layer structure. The IAM samples carried out at different temperatures annealing process and the sheet resistance and transmittance was improved up to  $12.5 \Omega/\square$  and 85.4%, respectively. The optimal annealing temperatures for the IAM sample are found to be at 200 °C, the IAM film with  $\text{Ag}_{75}\text{Mg}_{25}$  has a transmittance of 83% and a sheet resistance of  $12.5 \Omega/\square$ . The corresponding figure of merit has a value of  $1.08 \times 10^{-2} \Omega^{-1}$ . In addition, the relative change in resistivity of the IAM sample following fatigue testing is improved due to the AM interlayer. When the Mg content and bending cycle increases, the relative change in resistivity would increase. The result ( $\Delta R/R_0 = 0.41$ ) of the IAM sample is lower than that of a pure ITO film ( $\Delta R/R_0 = 0.93$ ).

Friday 6 July morning - 11:30/12:45

Parallel Session 2  
**METALLIC GLASSES XII**  
B.S. Murthy, Chair

ID-93

**Serrated flow during inhomogeneous deformation of bulk metallic glasses: from self-organized critical to chaotic dynamics***M. Khanouki<sup>1</sup>, R. Tavakoli<sup>2</sup>, H. Aashuri<sup>2</sup>*<sup>1</sup> *Sharif University of Technology*<sup>2</sup> *Materials Science and Engineering Department, Sharif University of Technology*

In this paper, the dynamic behavior of serrated flows observed in the flexural stress-deflection curves during three-point bending (3PB) tests on Zr-, Ti- and La-based bulk metallic glasses (BMGs) was statistically analyzed. Furthermore, the effect of test temperature and strain rate on the serrations was studied. Based on the ductility of alloy, two distinct types of dynamics are detected. For more ductile alloys (Zr- and Ti-based BMGs) the stress drop magnitude of serrations obeys a power-law distribution of shear avalanches, which is an indicator of the self-organized critical (SOC) state in dynamics. In this case, the size of avalanches has no characteristic scale. In contrast, the size of serrations corresponding to the less ductile alloy (La-based BMG) exhibits a characteristic length scale and implies that the underlying dynamics is chaotic. Results indicate that the plasticity in less ductile alloy can be related to the stick-slip process of few shear bands, but in the case of more ductile alloys, that can be attributed to the simultaneous nucleation and interaction of a large number of shear bands. Below a critical temperature or above a critical strain rate the serrations on flexural stress-deflection curves remove and a transition occurs from serrated to non-serrated plastic flow. This phenomenon is accompanied by changes in strain rate sensitivity (SRS) from negative to positive values. The comparison of apparent activation energy for the onset of serrated flow and the STZ activation energy indicates that these two processes are interrelated. Thus, at above critical temperature (or below a critical strain rate) the diffusional relaxation processes and the activation of STZs take place simultaneously, leading to serrated flow during inhomogeneous deformation.

**ID-360****Creating single element metallic glasses from molecular dynamics simulations**

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Theoretically single element metallic glasses would possess an interesting range of properties which could find applications in large number of industries including electronics, automotive, sensing and more. But it has been long thought that single element metallic glasses could not be produced. However experiments using nanotips with extreme cooling rates ( $1 \times 10^{14}$  [K/s]) have revealed that it is indeed possible to produce single element metallic glasses for a large number of bcc elements including Ta, Mo, W and V. But the production of single element MGs for fcc elements such as Au, Ag, Cu cannot easily be achieved. In this study, molecular dynamics has been used to rapidly cool single elements from the melt at different cooling rates. The results may be used as a guide in order to determine the relative glass forming ability by inspection of the resulting TTT diagrams.

ID-371

## Comparative analysis of thermodynamically predicted glass forming compositions with amorphous Ca-Mg-Cu alloy system

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<sup>2</sup> Department of Metallurgical and Materials Engineering, Visvesvaraya National Institute of Technology, Nagpur- 440010, M.S., India

The vague nature of physics inherent in glass forming ability (GFA) among the metallic glasses has led to the development of various parameters and its correlation with the different properties. Numerous experimental results have revealed that the thermodynamics and kinetic parameters play an important role in designing glass forming compositions with good GFA. Therefore, the thermodynamic modeling is used successfully in identifying glass forming compositions in Ca-Mg-Cu alloy in present study. Thermodynamic parameters PHSS and PSS derived from enthalpy of chemical mixing ( $\Delta H_{(\text{chem})}$ ), normalized mismatch entropy ( $S_{\sigma}/k_B$ ), and normalized configurational entropy ( $S_c/R$ ) has been used as GFA parameters. Further, variation of PHSS with calculated and reported compositions is evaluated. It is observed that with increase in Ca content, PHSS decreases. Similarly, with increase in Mg and Cu content, PHSS increases. Variation of PHSS with thermal stability ( $\Delta T_x$ ) and critical size ( $Z_c$ ) reflects linear sensitivity. Also, linear correlation is noticed between  $\Delta T_x$  and  $Z_c$ . Furthermore, variation of PHSS with instability parameter ( $\lambda$ ) is studied. It is observed that the former is as important as the latter but dominates in terms of compositional dependency. On the other hand, variation in PSS with  $\Delta T_x$ ,  $Z_c$ ,  $\lambda$  is also investigated and found identical results as that with PHSS. All these observations are compared and explained with the existing results. Owing to this PHSS can be promoted as the decisive parameter for designing bulk metallic glass (BMG) compositions with good thermal stability and maximum possible casting thickness of the alloy. The approach suggested here would allow one to get a reasonable prediction about the compositions having amorphous phase.

ID-403

**Measurement of the internal shear stress by nanoindentation tests in plastically deformed  $Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$  bulk metallic glass***Z. Kovács<sup>1</sup>, M. Abbas<sup>2</sup>, J. Lendvai<sup>1</sup>*<sup>1</sup> *Department of Materials Physics, Eötvös University, Budapest, H-1518, P.O.B. 32, Budapest, Hungary*<sup>2</sup> *Metallurgy and material science test lab (MMST), physics department, Faculty of Science, South Valley University, Qena, Egypt*

$Zr_{44}Ti_{11}Cu_{10}Ni_{10}Be_{25}$  bulk metallic glass samples have been deformed plastically by free end torsion tests at room temperature. After small plastic shear strain ( $\gamma \approx 0.01$ ) has been reached in a sample, it has been unloaded and its different cross-sections have been investigated by nanoindentation tests. Elastic core and plastically deformed perimeter of the deformed sample can be separated in cross-sections aligned off from the torsion axis. Variation of the hardness along the principal axis of the off aligned cross-section approximates the internal shear stress which can be determined from a simple elastoplastic model. Deviations of the experimental stresses from the macroscopic model indicate inhomogeneity of the internal stress field due to individual shear bands.



ID-430

**The role of topologically closed-packed structures in the phase transitions of Ta**Z. Wu<sup>1</sup>, Y. Mo<sup>2</sup>, Y. Liang<sup>3</sup>, Q. Xie<sup>3</sup>, Z. Tian<sup>1</sup><sup>1</sup> School of Physics and Electronics, Hunan University, Changsha 410082, China<sup>2</sup> School of electronic and communication engineering, Changsha University, Changsha 410003, China<sup>3</sup> School of Big Data and information engineering, Guizhou University 550025, China

Understanding the structure and glass forming ability (GFA) of metals is crucial to establishing metallic glass theory and producing advance materials with excellent properties. Recent experiment revealed that metal Ta can transfer between amorphous and crystalline solids by using nanosecond laser. Here we conducted several rapid cooling processes for pure Ta with the cooling rate in the vicinity of the critical values for vitrification and crystallization by classic molecular dynamics simulation to investigate the structural compatibility of metallic glasses and crystals. It is found that as cooling rate more than  $4.0 \times 10^{11}$  K/s, the system energy evolution can be fitted by two lines; while the system energy evolution does not appear an obvious drop-off (for crystallization) until cooling rate decreases to  $2.0 \times 10^{11}$  K/s; therefore, four cooling processes at cooling rates of 0.4, 0.3125, 0.25, and 0.2 K/ps are extensively investigated. Structure analysis reveals that the final solids obtained with cooling rate more than 0.2 K/ps include local crystalline regions; however, the size of local crystalline regions is independent with cooling rate, i.e., a higher cooling rate does not result in smaller local crystalline regions, and vice versa. The most interesting is that either in amorphous or crystalline solids the energy of the center atom of icosahedrons (Z12) is much higher than that of other local structures. Such local structures are defined as topologically close-packed units in which only exist tetrahedron interstices, and can be denoted by concise index, such as Z14, Z15 and A13. Further analysis indicates that TCP structures are not only the essential structural characteristic of metallic glasses, but also the link of various condense states of Ta such as liquid, super liquid, superheated solids, and different solids.

Friday 6 July morning - 11:30/12:30

Parallel Session 3  
**MECHANICAL PROPERTIES IV**  
E. Campari, Chair

**ID-69 (Invited)****Ti-based metallic glasses reinforced Al alloy matrix composites**

*Z. Wang<sup>1</sup>, W. Zhang<sup>1</sup>, K. Prashanth<sup>2</sup>, C. Suryanarayana<sup>3</sup>*

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*3 Department of Mechanical and Aerospace Engineering, University of Central Florida*

Metallic glass-reinforced Al matrix composites are an emerging new class of composite materials [1-4]. In this work we report a novel aluminum alloy composite reinforced with Ti-based metallic glass nanoparticles, which shows good tensile properties. The composite was fabricated by powder metallurgy through mechanical alloying combined with hot extrusion. During ball-milling process, metallic glass microparticles were refined into nano-sized particles owing to severe plastic deformation experienced by them [5]. Hot extrusion resulted in a dense and uniform dispersion of the metallic glass nanoparticles in the aluminum alloy matrix. This unique homogeneous structure resulted in a significant enhancement of strength without adversely affecting the plasticity, thus developing super-high specific yield strength. Some micro sized MG particles were remained in the 7075Al alloy matrix, which can deteriorate the plasticity. A critical analysis of the different factors contributing to the strength of the composite was carried out. It was shown that grain refinement, Orowan strengthening, and dislocation-dislocation interactions were the most important contributor to the enhanced strength of the nanocomposite.

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ID-129

**Fatigue properties of nanocrystalline Cu films on a flexible substrate**

B. Zhang

*Key Laboratory for Anisotropy and Texture of Materials, Ministry of Education, School of Materials Science and Engineering, Northeastern University*

Fatigue at small scales is a key issue for the long-term reliability of micro/nano-devices. Recent investigations on fatigue behaviour of thin metal films have shown a strong dependence of fatigue properties on length scales. The physical origin for fatigue size effects was attributed to the suppression of cyclic strain localization, leading to the gradual disappearance of typical bulk-like fatigue extrusions/intrusions. Although these investigations provide a deep insight into the fatigue mechanism of thin metal films with micron or submicron-scale grains, less work on fatigue properties of nanocrystalline metal films has been conducted.

In this study, nanocrystalline Cu films with different thicknesses ranging from 25 nm to 250 nm were deposited on a 125  $\mu\text{m}$ -thick polyimide substrate by a magnetron sputtering system. A comparative investigation of fatigue properties of the Cu films as-deposited and annealed were conducted under total strain control at room temperature. Variation in microstructures of the fatigued samples and fatigue damage behavior were characterized by transmission electron microscope (TEM) and high-resolution electron microscope.

The results show that the fatigue strength of the nanocrystalline Cu films as-deposited and annealed increases with decreasing the film thickness, which reveals a similar trend to that found in the Cu and Ag films with grain size about micron or submicron-scales. Furthermore, TEM observations reveal that grain growth occurred in the as-deposited films after fatigue. For comparison, the grain sizes in the annealed films and the annealed films subjected to fatigue loading were also examined at the same time. Evidently different extent of grain growth in the films was found. In addition, the size of the grains containing twins in the as-deposited and annealed films, and that after fatigue loading was also characterized. The variations in fatigue strength and grain growth behavior with film thickness are discussed. The results may provide a further understanding of fatigue behavior of nanocrystalline metal films.

ID-146

**Development of a titanium metastable alloy with promising mechanical properties for self-expandable stent applications***A.H. Plaine, M.R. da Silva, C. Bolfarini**Federal University of São Carlos*

Metastable titanium alloys with non-toxic elements have become promising metallic materials in biomedical applications due to their excellent haemocompatibility together with good mechanical, corrosion properties and cold formability. These alloys have been exploited with great perspective to pursue a concurrently low elastic modulus and high strength in order to minimize the “stress shielding” problem as well as to be used in soft tissue repair such as intravascular self-expandable stents. In this work, an attempt was made to combine theoretical composition design and thermo-mechanical treatments to produce a  $\beta$ -type titanium alloy with mechanical compatibility for self-expandable stents applications. By alloying, cold rolling and low temperature aging, metastable  $\beta$ -type Ti29Nb13Ta4.6Zr (wt. %) thin-wires with an elastic modulus of 46 GPa and an yield strength of 920 MPa were successfully fabricated. This combination of high yield strength and comparatively ultralow elastic modulus resulted in enhanced elastic (recoverable) strain of 2.0%, which is much higher than that of the conventional metallic stent materials. From optical microscopy, XRD, SEM and TEM, the microstructure responsible for the much sought-after mechanical properties was observed to be mainly consisted of an homogeneous distribution of nano-sized  $\alpha$ -precipitates in a  $\beta$ -phase matrix obtained via a spinodal decomposition of the pre-existed  $\alpha''$ -phase (martensite) through  $\alpha'' \rightarrow \alpha'' \text{ lean} + \alpha'' \text{ rich} \rightarrow \alpha + \beta$ . The  $\alpha$ -precipitates increases the strength of the material by impeding the motion of dislocations (spinodal hardening) while the  $\beta$ -matrix with relatively low content of  $\beta$ -stabilizers gives rise to the observed ultralow elastic modulus. More broadly, these findings could be extended to developing advanced metastable  $\beta$ -type titanium alloys for implants and other engineering applications.

Friday 6 July morning - 11:30/12:45

Parallel Session 4

**APPLICATION II**

M. Alvador-Fernandez, Chair

ID-482

**Selective oxidation of benzyl alcohol catalyzed by CeO<sub>2</sub>-nanorods supported palladium***S. S. Moeini<sup>1</sup>, D. Tofani<sup>1</sup>, I. Luisetto<sup>2</sup>, S. Tuti<sup>2</sup>*<sup>1</sup> *Laboratory of Organic Chemistry, Department of Science, University of Roma Tre, Rome, Italy*<sup>2</sup> *Laboratory of Chemistry of Materials with Catalytic Properties, Department of Science, University of Roma Tre, Rome, Italy*

Selective oxidation of benzyl alcohol (BA) to benzaldehyde (BZ) is considered as a crucial functional group transformation, since the product is a key intermediate for the synthesis of fine chemicals, in the perfume, pharmaceutical and dyestuff industries [1,2]. This oxidation reaction is convention-ally performed by various stoichiometric oxygen donors such as chromates, permanganates, and peroxides which are expensive and highly toxic [3,4].

Therefore, from environmental point of view, and to reduce the overall production cost, there is a great interest in the development of heterogeneous catalysts capable of utilizing air or oxygen as greener oxidants. In this way, various issues such as catalyst deactivation and BZ selectivity must be overcome for the industrial implementation of this reaction. In present research work, the selective oxidation of BA to BZ is studied using Palladium supported on CeO<sub>2</sub> Nanorods (NR) as catalyst, and atmospheric air as a green oxidant. CeO<sub>2</sub>-NR were prepared hydro-thermally [5], then Palladium oxide was deposited by wet-impregnation on CeO<sub>2</sub>-NR using Pd(NO<sub>3</sub>)<sub>2</sub>•2H<sub>2</sub>O and calcination at 400 C° (PdO/CeO<sub>2</sub>-NR). Structural, morpho-logical and properties of the synthesized materials were studied by mean of XRD, TEM, SEM, and BET methods. Catalytic oxidation of benzyl alcohol using PdO/CeO<sub>2</sub>-NR was conducted in toluene and in ethanol solvents under air flow (20ml/min). Effect of temperature (60-110 C°), BA concentration and catalyst/BA ratio (1/1, 2/1, 3/1) on catalytic activity and BZ yield was studied. Reactant and products were analyzed by GC-MS. The results showed that in toluene, catalyst deactivation occurred and high BZ yield was not achieved. In ethanol as solvent, BZ was produced with up to 99% yield and considerable selectivity. The oxidation rate increased with the catalyst/substrate ratio and with the BA concentration.

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**ID-160****Influence of the correction to the Wills-Harrison approach on the thermodynamics of liquid transition-metal binary alloys**

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Some years ago, we applied the Wills-Harrison (WH) [1] approach in conjunction with the variational method of the thermodynamic perturbation theory to calculate thermodynamic properties of Fe-Co and Fe-Ni liquid alloys [2, 3].

Later, we introduce the correction to the WH model due to the non-diagonal coupling between d electrons on different atoms and applied this correction to investigate the WH effective pair interactions in liquid Fe, Co and Ni [4].

Here, the influence of this correction on the thermodynamics of Fe-Co, Fe-Ni and Co-Ni liquid alloys near their melting temperatures at different component concentrations is studied.

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ID-202

**Local structure near a Ni atom in a rapidly quenched Al<sub>0.3</sub>CrFeCoNi high entropy alloy**

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High entropy alloys (HEAs) are promising for new structural materials, because they possess both ultra-high strength and high ductility. Ultra-high strength of HEAs is often explained by solid solution strengthening. In this study, we demonstrated X-ray fluorescence holography (XFH) experiments for an Al<sub>0.3</sub>CrFeCoNi HEA with the face-centered cubic (FCC) structure to examine local structure near a Ni atom.

XFH is one of atomic resolution holography techniques, which can directly reconstruct three dimensional atomic images from holograms. XFH experiments were performed using synchrotron radiation at BL13XU in SPring-8. Holograms were recorded by inverse mode at room temperature. XFH experiments were performed on the same large grain in a rapidly quenched Ar arc-melted ingot after one week (as-prepared) and after one year aged at room temperature. Atomic images were reconstructed in planes parallel to {111} by slicing three dimensional atomic images obtained by Fourier transformation of the holograms.

Standing waves were clearly observed in the holograms recorded for the as-prepared specimen, while they were hardly found in the holograms recorded after one year. It implies that any structural change is taken place in the specimen during one year at room temperature. Most atomic images were reconstructed near lattice points of FCC for the as-prepared specimen and the aged specimen. Thus, the local structure near a Ni atom in Al<sub>0.3</sub>CrFeCoNi HEA almost keeps the FCC structure. However, reconstructed atomic images for the as-prepared specimen also revealed that the fourth nearest atoms of a Ni atom displace about 40 pm along <110> in a {111}, which corresponds to the primary slip system of FCC metals. Dependence of Vicker's hardness as a function of aging period at room temperature will be also reported.

ID-375

**Thermoluminescence of carbon quantum dots doped aluminium oxide exposed to X ray and UV radiation***C. Gomez Solís, M. Hernández, J. Alvarado, M. Aquino, P. Ramírez**Universidad de Guanajuato*

Aluminum oxide ( $\text{Al}_2\text{O}_3$ ) is a ceramic material with desirable features as chemically inert, is abundantly available and presents interesting optical properties like Photo-luminescence (PL), Optically Stimulated Luminescence (OSL) and Thermoluminescence (TL), these last two phenomena are suitable for radiation detection.  $\text{Al}_2\text{O}_3:\text{C}$  is a reference material in OSL and TL radiation dosimetry, then, any development or enhancing of this material is an emergent topic. Due these facts we present a nanocrystalline  $\text{Al}_2\text{O}_3:\text{C}$  powder, synthesized by the polyester-combustion method for Ultra-Violet Radiation (UVR) and diagnostics X ray detection. As well several characterization studies were performed: evolution of crystalline phases of obtained powders was accomplished through X-ray diffraction, micro-Raman spectroscopy, in addition to visible ultraviolet spectroscopy and using a scanning electron microscope (SEM) it was examined surface, morphology and impurity content of the  $\text{Al}_2\text{O}_3:\text{C}$ . The single-phase  $\text{Al}_2\text{O}_3:\text{C}$  powder was obtained after heat-treatment at  $-C$  (study of the particles was accomplished through measures of crystallite and the particle size). This analysis suggested that the presence of carbon quantum dots in the amorphous phase of  $\alpha\text{-Al}_2\text{O}_3:\text{C}$  and  $\gamma\text{-Al}_2\text{O}_3:\text{C}$  has an effect on the morphology of the particles obtained in addition to stimulating the thermoluminescent response of alumina after UV and X ray exposure as it show glow curves analysis.

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**ID-313****Effect of Ag decorated MWCNTs on mechanical reliability of Sn-58wt%Bi solder**

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The electronic industry relies on Pb-free solders because lead can have harmful effects on the environment and human health. One of the important requirements for electronics solders is processing temperature as low as, or lower than Sn-Pb solder. A representative low-temperature Pb-free solder, Sn-58 wt%Bi solder, has been considered as a highly promising candidate because of its high tensile strength and good creep resistance. The Sn-58 wt.% Bi solder has low melting point, however it has poor ductility and shock absorbance. Various approach has been tried to enhance the mechanical properties of the Sn-58Bi solder. An attractive approach to improve the mechanical property of the solder joint is application of Carbon Nanotube (CNT) due to their outstanding mechanical, electrical and thermal property. In CNT, Multi-Walled Carbon Nanotube(MWCNT) has been used widely as a structural material because of its advantage in mass production and low cost. However, MWCNTs have a low density, causing a big density difference and weak bonding characteristics with solder matrix, which leads to a severe segregation problem and non-uniform dispersion during reflow process. Thus, Ag-decorated MWCNT(Ag-MWCNT)s are proposed to solve these segregation problems. We Investigated Mechanical properties and morphology of intermetallic compound (IMC) of Sn<sub>58</sub>Bi solder including various Ag decorated MWCNTs contents (0, 0.05, 0.1 and 0.2 wt.%). The Ag decorated MWCNT used in experiment were synthesized with acid treatment. Sn-58Bi solder pastes including Ag decorated MWCNTs were printed on the printed circuit board (PCB) with organic solderability preservative (OSP) surface finish, and then the joints were aged at 105 °C for up to 100, 300, 500 and 1000 hours. The shear test was conducted to evaluate the mechanical property of the solder joints. The shear strength increased about 15% with 0.1 wt.% Ag-decorated MWCNTs. The thickness of IMC of Sn-58Bi solder increased with increasing aging time.

Friday 6 July afternoon - 14:30/15:15

Parallel Session 1  
**NANOSTRUCTURED MATERIALS XIV**  
A. D'Elia, Chair

ID-266

**Impact of the additives stoichiometry on the properties of HAp/TiO<sub>y</sub> nanocomposite***S. Rempel<sup>1,2</sup>, A. Valeeva<sup>1,2</sup>, D. Eselevich<sup>1</sup>, A. Rempel<sup>1</sup>*<sup>1</sup> Institute of Solid State Chemistry, Ural Branch of the RAS<sup>2</sup> Ural Federal University named after the First President of Russia B.N. Eltsin

The development of methods for the nanomaterial synthesis allows designing new systems for medicine and biology. It has been reported that titania and hydroxyapatite (HAp) present a good combination for functionally graded materials and provide a gradient of bioactivity and good mechanical properties [1].

In present work the effect of titanium monoxide TiO<sub>y</sub> on properties of HAp was evaluated. Nanoparticles of titanium monoxide with different mass content and stoichiometry (10 or 20 wt. % of sub-stoichiometric TiO<sub>0.92</sub> or superstoichiometric TiO<sub>1.23</sub>) were added to HAp. Pressed pellets were annealed in vacuum (10-3 Pa) quartz ampules at temperatures of 400, 600 and 800°C for 4 h. The initial materials and composites were studied in detail at different stages of heat treatment with the use of XRD analysis, SEM, pycnometry, microhardness measurements [2], IR and Raman spectroscopy methods.

In the process of annealing of HAp/TiO<sub>y</sub> nanocomposites from room temperature to 600°C, new phases Ti<sub>4.5</sub>O<sub>5</sub> and TiO<sub>2</sub> are formed (depending on the stoichiometry of additives). At the first stage (400°C), the surface groups [Ti(OH)<sub>2</sub>]<sup>2+</sup> and [TiHPO<sub>4</sub>]<sup>2+</sup> are formed, and partial cation heterovalent substitution of Ti<sup>3+</sup> and Ti<sup>4+</sup> for Ca<sup>2+</sup> takes place, which is accompanied by vacancy formation and anion substitution. As the annealing temperature is raised to 600°C, the surface groups disappear. It is shown that doping of HAP by TiO<sub>y</sub> of the different stoichiometry and weight content allows directionally changing the properties of the composite material, in particular, to manage the processes of phase formation.

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ID-268

**Adsorption of xanthine on citrate-stabilized gold nanoparticles**S. Caporali<sup>1</sup>, F. Muniz-Miranda<sup>2</sup>, M. Muniz-Miranda<sup>1</sup><sup>1</sup> Department of Chemistry "Ugo Schiff", University of Florence, Via Lastruccia 3, 50019 Sesto Fiorentino, Italy<sup>2</sup> Center for Molecular Modeling (CMM), Ghent University

Gold nanoparticles have attracted much attention in the field of nanotechnology due to their many chemical and biomedical applications [1], in sensing, catalysis, drug delivery, imaging, and nonlinear optical processes. This is due to their peculiar properties, which can be summarized in this way: marked chemical and physical stability; high biocompatibility; efficient surface functionalization with organic and biological ligands; enhanced optical responses related to surface plasmons. The most common procedure to obtain stable aqueous suspensions of gold nanoparticles is the reduction of tetrachloroauric acid by sodium citrate [2,3]. The role of citrate anions in the formation of nanosized gold particles was argument of different experimental and theoretical studies [4,5], even if the type of interactions between citrate and gold and the effect on the stabilization and reactivity of the nanoparticles are not yet clarified. Among studies in nanomedicine using gold nanoparticles, those concerning the detection of DNA/RNA chains and their nucleobases [6-8] play a central role.

Here, we have studied the adsorption of xanthine, a nucleobase present in human tissues and fluids and involved in metabolic processes, on citrate-reduced gold colloidal nanoparticles, by means of SERS and XPS measurements. In particular, the SERS-activation of xanthine/gold nanoparticles in the near-infrared spectral region, where fluorescence usually does not occur, and the role of the citrate anions in the aggregation of the gold particles and in the adsorption of the ligand molecules have been analyzed.

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**ID-298****Synthesis of nickel ferrite by CTAB assisted hydrolytic stripping***A.J. Muñoz, E.G.P. Beas**Instituto Politécnico Nacional-ESIQIE, Depto. de Ingeniería en Metalurgia y Materiales*

In the present study, nickel ferrite has been successfully synthesized by hydrolytic stripping in the presence of CTAB ( $0.5 \times 10^{-4}$ ,  $2 \times 10^{-3}$  and 0.05 M) at several reaction times (15, 30, 45 and 60 minutes). The magnetic material was processed by hydrolytic stripping, in the presence of the surfactant, of Ni and Fe(III) carboxylates obtained by solvent extraction using naphthenic and Neodecanoic® acids and maintaining a Fe/Ni = 2 ratio. According to ICP-OES, FTIR, MEB, DRX and VSM results, nickel ferrite precipitates as the only phase, independently of either reaction time or concentration of the surfactant. In addition, the surfactant acts discretely in the preservation of particle size and morphology, but impacts highly during the reaction.

Friday 6 July afternoon - 14:30/15:30

Parallel Session 2  
**METALLIC GLASSES XIII**  
J. Bhatt, Chair



**ID-471****Effect of ultrasonic vibration on the microstructure and mechanical properties of a Zr-based bulk metallic glass***S. Li*

In this work, the effect of ultrasonic vibration on the structure and mechanical properties of a Zr-based bulk metallic glass has been investigated. After long-time ultrasonic vibration at room temperature, the sample still retains a fully amorphous structure and exhibits higher hardness and Young's modulus. The high-resolution transmission electron microscopy in conjunction with auto-correlation function analysis demonstrates that structural heterogeneity can be modified by ultrasonic vibration. The results indicate that ultrasonic vibration can be developed as a useful tool to tune the microstructure and mechanical properties of metallic glasses.

ID-189

## Characterization of heterogeneities in a CuZr based bulk metallic glass after high pressure torsion deformation

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Bulk metallic glasses (BMGs) are an exciting new class of materials. Outstanding mechanical properties such as e.g. their high elastic limit and corrosion resistance render them especially interesting for application as structural materials. Unfortunately, these desired properties come with the drawback of almost non-existing tensile ductility, caused by strain softening and thereby localization of plastic deformation into narrow shear bands. Tailoring ductility in BMGs remains a scientific challenge up to date, although significant progress in understanding the amorphous structure and its impact on the deformation behavior has been made [1]. A promising method to overcome the ductility limitation is severe plastic deformation using high pressure torsion (HPT) [2]. This pre-processing method rejuvenates the amorphous structure by introduction of excess free volume and thereby increases the ductility.

Here, we combine structural and mechanical results to obtain a full characterization of CuZrAlAg BMG processed by HPT. Nanoindentation and synchrotron X-ray diffraction studies conducted on cross-sectional samples of the HPT discs yield a 2-dimensional map of mechanical and structural properties. Depending on the HPT condition (number of rotations, hydrostatic pressure, temperature) a more or less sharp structural gradient over the height of the HPT disc evolves. Hardness and Young's modulus show a large drop of up to 25% in the strain softened regions, as compared to the as-cast state. The change in plastic response was studied by statistical analysis of the discontinuous deformation, as well as by creep measurements at maximum load during nanoindentation. While the number of detectable discontinuities decreased, the creep is increased for highly strained regions. Synchrotron X-ray diffraction studies reveal an increase in average atomic volume, confirmed by relaxation measurements performed using differential scanning calorimetry. An increase in the full width at half maximum of the first intense diffraction ring indicates an increased structural heterogeneity. These structural modifications after HPT are directly linked to the change in mechanical properties.

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ID-176

**Magic oxygen in metallic glasses: tuning Cu-Ag porous nanomembrane into nanoporous Ag-Cu@Ag core-shell alloy***X. Liu<sup>1</sup>, K-F Yao<sup>2</sup>*<sup>1</sup> *Institute of Materials, China Academy of Engineering Physics*<sup>2</sup> *Tsinghua University*

Metallic glasses (MGs) have uniform amorphous structure, which enables them to be suitable materials for preparing nanoporous structures by dealloying. Efforts have been paid for the composition design of MGs to obtain nanoporous structures with enhanced performance. These attempts mainly focus on the adjustment of the noble and base metals, while the intrinsic mechanism of the dealloying process is consistent. In present study, we firstly introduce oxygen into the  $Zr_{48}Cu_{36}Ag_8Al_8$  MG ribbon to develop a Zr-Cu-Ag-Al-O amorphous/crystalline composite. Compared with the simple Cu-Ag bimetallic porous nanomembranes (PNMs) by directly dealloying the  $Zr_{48}Cu_{36}Ag_8Al_8$  MG, hierarchically nanoporous Ag-Cu@Ag core-shell structure were successfully synthesized by chemical dealloying of the newly developed Zr-Cu-Ag-Al-O alloy. The inclusion of oxygen in MGs has played the magic and important role in determining the eventual product, which changes the intrinsic mechanism of the dealloying process by enabling the dissolution and re-deposition of copper, and finally tunes the Cu-Ag PNM into the nanoporous Ag-Cu@Ag core-shell alloy. The resulting Ag-Cu@Ag core-shell structure consists of small nanopores of  $\sim 15$  nm, large nanopores of  $\sim 40$  nm and ligaments of  $\sim 60$  nm. Compared with the Cu-Ag PNM, the nanoporous Ag-Cu@Ag core-shell alloy exhibits enhanced oxidative stability as well as antibacterial activity against *E. Coli* DH5 $\alpha$ . Our results provide a new way to prepare metallic core-shell nanostructures by a one-pot method, and offer important insights on the discovery and design of complex nanostructures for achieving enhanced performance.

ID-402

**Nonlinear metallic glass flat springs**

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Metallic glasses show a wide elastic strain range on the order of 2% before the onset of plastic deformation. By exploiting their high elastic limit, it is found that under load sinusoidal waves can be induced mechanically on an arc shaped metallic glass foil by its initial shape multiplication [1]. Provided that the deformation remains in the elastic region, this undulative behaviour is reversible, functioning as a flat spring with multiple spring constants and high fatigue resistance [2]. Furthermore, rapid annealing of elastically deformed metallic glasses without thermal embrittlement (thermo-elastic forming) offers unique opportunities for producing metallic glass foils with complex geometries [3,4]. The geometrical characteristics of shaped metallic glass foils in wavy patterns can be designed so that their unusual reversible sinusoidal behaviour is utilised for the development of multi-functional amorphous metallic flat springs for applications including sensors and actuators.

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Friday 6 July afternoon - 14:30/15:45

Parallel Session 3  
**MECHANICAL PROPERTIES V AND APPLICATIONS III**  
P. Konda Gokuldoss

## ID-68

**Ductility improvement mechanism of pure titanium with oxygen solid solution after water quenching**

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Oxygen solid solution is well known to improve the mechanical strength of Ti and its alloys, while it also imposes a serious embrittlement effect. This study clarified the water quenching (WQ) effect after heat treatment on the microstructures and mechanical properties of powder metallurgy (PM)  $\alpha$ -titanium (Ti) material with dissolved 2.76 at.% O was investigated in detail and effective for a significant improvement of the strength and ductility. For example, the extruded PM Ti rod with uniform oxygen solution atoms, having  $\alpha$ -Ti grains with about 10  $\mu\text{m}$  in diameter, was fabricated by using the elemental mixture of pure Ti and  $\text{TiO}_2$  powders. Subsequently, the water quenching was applied to the Ti rod after isothermal annealing at 1173~1373 K. Tensile test results at the ambient temperature indicated that ultimate tensile strength (UTS) of the specimens after WQ at 1223 K and 1273 K, where Ti-2.76 at.% O material had  $\alpha+\beta$  dual phases, was 993 MPa and 988 MPa while that of as-extruded Ti rod without WQ was 1079 MPa. On the other hand, the elongation to failure of the quenched ones at 1223 K and 1273 K was 12.5% and 19.1%, respectively. They are significantly higher than that of as-extruded Ti rod with 6.0% elongation. The Ti-2.76 at.% O materials with the above QW treatment consisted of equiaxed  $\alpha$ -grains with about 30  $\mu\text{m}$  in diameter, and some martensite phases were also detected at the grain boundaries. In addition, they had orientation misfits in  $\alpha$ -Ti grains, which were formed on the interfaces between  $\alpha$  and  $\beta$  phases during phase transformation in WQ due to a lower oxygen content in primary  $\beta$  phases compared to the primary  $\alpha$  phases.

ID-460

## Hydrogen diffusivity and solubility and interaction with microstructure of $\text{Fe}_{20}\text{Mn}_{20}\text{Ni}_{20}\text{Co}_{20}\text{Cr}_{20}$ and $\text{Fe}_{22}\text{Mn}_{40}\text{Ni}_{30}\text{Co}_6\text{Cr}_2$ High entropy alloys

A. Castilho, D. Santos, J. Belo, S. Marques

PENT-COPPE/UFRJ

In recent years, numerous metallic alloys have been increasingly used in extreme conditions, which can combine high pressure and high temperature, exposure to various gases ( $\text{H}_2\text{S}$ ,  $\text{CO}_2$ ,  $\text{H}_2$  ...) sea-water under cathodic protection. These agents can lead to decreased lifetime in service of metallic alloy, mainly when plastic or elastic stress are applied. These extreme conditions, the hydrogen has been one of the most dangerous because of its deleterious nature. In this context, to find alloys capable of combining high mechanical resistance and corrosion, in addition to solubilize large amount of hydrogen, without become brittle, has been the great challenge to researchers in many research center nowadays.

A new concept of equiatomic single-phase alloys that is called High Entropy alloys, HEA, with at least 5 elements is singled out as promising to replace conventional high resistant steels and super-alloys. The HEA have pay attention as its performance with respect its mechanical properties. These alloys can be designed with the aid of CALPHAD technique that allows the study of phase diagrams, based on thermodynamic aspects. Recent developments point out to the possibility of using alloys with non-equiatomic compositions and even containing small amount of second phases which in principle act contributing to increase the mechanical strength of the alloy. The classical structure of alloys HEA is a crystalline composed of atoms in complete solid solution with a great mismatch which helps to increase the configurational entropy. This atomic disorganization can provide the existence of sites with different level of potential energies in order to solubilize more stable large amounts of hydrogen. The aim of this work is study the hydrogen diffusivity, solubility and inter-action with the microstructure of the alloys:  $\text{Fe}_{20}\text{Mn}_{20}\text{Ni}_{20}\text{Co}_{20}\text{Cr}_{20}$  and  $\text{Fe}_{22}\text{Mn}_{40}\text{Ni}_{30}\text{Co}_6\text{Cr}_2$ . Samples were prepared by arc melting furnace and then cold worked. The alloys were submitted to HPT to produce nanocrystalline structure and measured by Thermal desorption spectroscopy, TDS. Both alloys present fcc structure and the hydrogen diffusivity very low  $10^{-15}$ -  $10^{-14}$   $\text{m}^2/\text{s}$  at room temperature. The gas hydrogen permeation test was performed from 300  $^\circ\text{C}$  to 500  $^\circ\text{C}$ . The energy level to hydrogen interaction of atoms of the alloy was calculated by Density functional theory, DFT using MedeA software. The hydrogen diffusivity and solubility are compared with Ni alloys at the present work.

## ID-39

**SnO<sub>2</sub> coatings on 304 stainless steel for corrosion protection**

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Nowadays, some materials, because highly demanding operative conditions, need to present a superior corrosion resistance. For example, it is well known that the marine environment is particularly aggressive to stainless steel. In this work, tin (IV) oxide (SnO<sub>2</sub>) coatings were synthesized by sol-gel method and deposited on 304 stainless steel (304 SS) by dip-coating technique. Tin (II) oxalate (SnC<sub>2</sub>O<sub>4</sub>) and distilled water (H<sub>2</sub>O) were used as precursor and solvent respectively. Powders were obtained and analyzed by Fourier Transformed Infra-Red Spectroscopy (FTIR) and X-Ray Diffraction (XRD) to determine the heat treatment temperature to the coatings and the crystal structure tetragonal cassiterite type; finally performed coatings were evaluated to compare their properties against corrosion process in a saline environment to 3 %wt. sodium chloride (NaCl) aqueous solution by potentiodynamic anodic polarization and polarization resistance. The results showed that the corrosion rate decrease  $\approx 99\%$  with respect to uncoated 304 SS.



**ID-199****Ti substituted alumina dispersion-strengthened Cu alloy fabricated via internal oxidation**

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Ti added alumina dispersed Cu alloy was fabricated via internal oxidation and consolidation methods, and the mechanical and electrical properties of the alloy was discussed based on the microstructure. Cu<sub>0.8</sub>Al and Cu<sub>0.6</sub>Al<sub>0.4</sub>Ti powders were mixed with oxidizer, and the mixtures were inputted in the copper cans. The specimens were internal oxidized at 800 C° and reduced in hydrogen atmosphere, and then extrude at 800 C°. All samples were annealed at 500 C° and drawn at room temperature to a 90% reduction in their cross-sectional area. The alumina-dispersed alloy with Ti addition showed higher values of conductivity, hardness and tensile strength than the alloy without Ti. Microstructure analysis via transmission electron microscope (TEM) and scanning electron microscope (SEM) revealed that Ti addition helps to reduce remained oxidizer dramatically after internal oxidation and effectively decrease the size of alumina. This interesting result might be occurred by addition of Ti, which helps oxidation reaction in the alumina dispersed Cu alloy, consequently oxidation reaction with active lead to simultaneously increase the strength and conductivity due to the decreased size of alumina and increment of purity in Cu matrix. A combination of tensile strength and conductivity of 500 MPa and 92.3% IACS, respectively, was achieved in the Cu-Al-Ti alloy after drawing with an 80% area reduction.