

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

### Room Pacific Salon 1 - Session H2-1-MoM

#### Fatigue and Wear

**Moderators:** Olivier Pierron, Georgia Institute of Technology, USA, Timothy Rupert, University of California, Irvine, USA

10:00am **H2-1-MoM-1 Acoustic Emission Measurements to Quantifying Damage Accumulation and Crack Initiation in Nickel Single Crystals during High Frequency *In Situ* Cyclic Loading Experiments**, *S Lavenstein, Jaafar El-Awady*, Johns Hopkins University, USA **INVITED**

We present a new methodology, coupling between acoustic emission measurements and high frequency *in situ* scanning electron microscopy experiments to quantify the evolution of damage and crack initiation in single crystal nickel microcrystals. The mechanical properties are continuously monitored during the cyclic loading using dynamic measurements and signal analysis. The experimental results show that persistent slip bands (PSBs) form in these microcrystals in the absence of any apparent dislocation dense regions as commonly observed in bulk crystals. In addition, the speed of propagation of these PSBs is measured. Quantification of crack initiation and propagation is also analyzed from acoustic emission measurements, and the statistics of these measurements at different stages of crack propagation (i.e. short crack and long crack regimes) are quantified.

10:40am **H2-1-MoM-3 A Data-driven Approach to Describe Fatigue Damage Evolution and Crack Initiation in a BCC Steel Microstructure**, *A Durmaz, Thomas Straub, C Eberl*, Fraunhofer IWM, Germany

A material's fatigue lifetime is determined by the crack formation process: damage accumulation in individual grains, micro crack initiation, and finally short crack formation. In the past years, a testing methodology for fatigue damage evolution investigation was developed. This methodology reduced samples sizes and cycled them at their resonant frequency, using sensitive measurements of the resonant frequency for correlation with damage initiation.

Building on this work, a multi modal approach has been developed employing in-situ optical images of the sample surface to better understand damage evolution kinetics and improve crack initiation analysis. The processed image data allows the creation of labels for machine learning (ML) methods, such as random forests, which are based on decision trees. As ML attributes various microstructure characteristics are extracted for each grain using complementing ex-situ EBSD measurements and MTEX. In order to generate a sufficient and balanced dataset the SEM and EBSD methods were automated.

11:00am **H2-1-MoM-4 Low and High Cycle Fatigue Testing of Ni Microbeams**, *Alejandro Barrios*, Georgia Institute of Technology, USA; *E Kakandar*, Cranfield University, UK; *X Maeder*, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; *G Castelluccio*, Cranfield University, UK; *O Pierron*, Georgia Institute of Technology, USA

Small-scale fatigue is an active area of research due to the widespread use of metallic films and micrometer-scale structures in applications such as flexible electronics, and micro electromechanical systems (MEMS). New techniques are required to characterize the fatigue damage and its size effects in metallic microcomponents under loading conditions relevant to their applications. This work presents two small-scale fatigue testing techniques to characterize the fatigue behavior of electroplated Ni microbeams subjected to in-situ high cycle and low cycle fatigue loading conditions. The in-situ high cycle fatigue technique consists of MEMS microresonators that are driven at resonance inside a Scanning Electron Microscope (SEM), leading to fully-reversed loading of microbeams at a frequency of ~8 kHz. The fatigue damage leads to a decrease of the microresonator's resonance frequency and is measured to quantify crack growth rates. The low cycle fatigue technique consists of the external mechanical actuation of the microresonator using a micromanipulator, which exerts a close to fully reversed bending fatigue loading on the microbeam. The micromanipulator is attached to a load cell and the decrease in load needed to actuate the device as cycling increases is used to characterize fatigue damage. Both techniques were complemented with Focused Ion Beam (FIB) cross sectioning that allow for a better understanding of the mechanisms of crack nucleation and propagation.

The crack propagation rates on the surface of the microbeam in the high cycle regime are extremely low (average values down to  $\sim 10^{-14}$  m/cycle) indicating that the fatigue mechanism in high cycle fatigue does not follow the common crack tip stress intensification. Instead, crack nucleation and propagation are caused by the formation of voids that nucleate from the condensation of vacancies. However, in the low cycle fatigue regime, the microbeam does follow the conventional fatigue mechanisms observed in literature. Results will highlight the comparison in fatigue life and mechanisms of the low cycle and high cycle fatigue regimes. In addition, further testing will evaluate the frequency effects by comparing low cycle and high cycle tests at similar stress amplitudes. Electron backscatter diffraction (EBSD) scans will also allow for a better understanding of the microstructural variation along the crack path in the microbeam.

Furthermore, modeling efforts with 3D crystal plasticity will complement experimental results by giving a more complete understanding of the stress/strain states at crack initiation sites and a prediction of the low cycle fatigue life of the microbeam at various loadings.

11:20am **H2-1-MoM-5 Nanocrystalline Alloys with Disordered Complexions Probed by In Situ Mechanical Testing**, *Timothy Rupert, J Wardini, J Schuler*, University of California, Irvine, USA

Recent innovations in materials processing have enabled the creation of nanostructured materials with unique grain boundary structures. Here, we focus on nanocrystalline metals with amorphous intergranular films, which have been predicted to add a toughening effect. Due to the limited volumes of materials that can be made on lab scales or the geometry of typical parts, it is difficult to accurately probe the mechanical properties of these materials. In this talk, we first describe the use of in situ mechanical testing in the scanning electron microscope, with the goal of measuring important properties only from the regions of interest. We focus on properties of fundamental importance, such as yield strength, strain hardening rate, ductility, and rate sensitivity, with measurements made by microtension and microcompression of very small samples. In addition, in situ fatigue testing inside of the transmission electron microscope provides an atomic scale view of plasticity near a developing crack in materials with and without the amorphous films. Using these results, we revisit the design of these materials, to suggest paths for improvement in the future.

11:40am **H2-1-MoM-6 Structural Evolution and Wear-rate Transitions in Nanocrystalline Alloys**, *Olivia Donaldson, J Panzarino, T Rupert*, University of California, Irvine, USA

Nanocrystalline alloys have shown great potential as wear resistant coatings due to their high strength and hardness, but cyclic plastic deformation associated with sliding contact can lead to grain coarsening. In this study, we explore near-surface microstructural changes resulting from scratch wear tests in a nanoindenter, with a focus on understanding how such evolution affects subsequent wear properties. Electrodeposited Ni-W films, with an initial grain size of 3 nm, underwent transmission electron microscopy characterization of the grain structure and texture following scratch wear under normal loads of 10 to 50 mN. Additional Ni-W films with a grain size of 45 nm, achieved through annealing, underwent wear testing as well to provide a contrasting example where damage appears as grain refinement. A clear connection between instantaneous wear rate and subsurface microstructure was found. In addition, the final grain size for the damage layer near the surface was observed to be strongly dependent on the applied normal force, suggesting that local stresses near the surface affect the metastable, near-surface grain size that forms during wear. Finally, a wear map which captures microstructural changes due to different experimental testing variables was constructed and preliminary experiments on Cu-rich alloys were performed to provide a comparison.

12:00pm **H2-1-MoM-7 Effects of Thermal Cycling on Nano-mechanical Properties of Thermal Barrier Coatings**, *Marco Sebastiani*, Roma TRE University, Italy

In the present work, we analysed the nano-mechanical properties of high- and low-porosity Ytria-partially stabilized zirconia – YSZ top coats and of the thermally grown oxide (TGO) layer in a thermal barrier coating (TBC), produced by thermal spray.

High-speed nanoindentation and micro-pillar splitting were used for spatially-resolved analysis of elastic modulus, hardness and fracture toughness of the materials as a function of the number of thermal cycles.

In this way, the degradation of both elastic modulus and hardness of the YSZ top-coat is quantified, and a correlation with observed microstructures is proposed.

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In addition, the micro-scale fracture toughness of the TGO layer is measured, for the very first time, as a function of the number of thermal cycles.

The existence of a critical TGO thickness of  $\approx 5 \mu\text{m}$ , postulated by previous research, is confirmed.

Until this threshold, the TGO is solely based on aluminium oxide, it grows slowly and generally remains dense and compact, except for some prominent asperities where the TGO becomes thicker. As a result, its micro-scale fracture toughness of the TGO also tends to increase up to maxima of  $2.5 - 3 \text{ MPa}\cdot\sqrt{\text{m}}$ .

These findings have implications on the failure mechanisms. Indeed, in addition to large stress concentrations along the interface, it is inferred that a reduction in the properties of both the TGO and the top coat contribute to failure of the TBC.

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

### Room Pacific Salon 1 - Session H2-2-MoA

#### Nanoscale Plasticity

**Moderators:** Timothy Rupert, University of California, Irvine, USA, Olivier Pierron, Georgia Institute of Technology, USA

#### 1:40pm H2-2-MoA-1 Assessing the Mechanical Properties of Thin Organic Semiconductor Coatings, Steve Bull, Newcastle University, UK

A wide range of organic semiconductor coatings have been developed for optical and electronic applications and have been extensively characterised for their electronic and optical properties. What mechanical measurements have been made are focused on assessing the average properties of a film (e.g. using buckling to assess elastic moduli) but are not suitable to assess point-to-point variation in mechanical response which may be related to changes in coating microstructure due to crystallisation and/or phase separation. The assessment of time-dependent mechanical response is also lacking. This presentation will address the challenges of testing 100-300nm thin films of a range of organic semiconductors on a glass substrate to extract mechanical properties using nanoindentation at very low loads (peak loads less than 50 $\mu$ N). The importance of surface contamination and adhesion of the tip to the film, the effect this has on setting the conditions of first contact and the effect this has on measured properties will be discussed. The use of extrapolation methods to determine coating only properties will be assessed for both quasi-static and dynamic measurement techniques. Finally the effect of coating microstructure and surface roughness on the measured results will be discussed.

#### 2:00pm H2-2-MoA-2 In Situ TEM Activation Volume Measurements, S Gupta, S Stangebye, J Kacher, Olivier Pierron, Georgia Institute of Technology, USA

Signature parameters such as true activation volume are often characterized to identify the governing plastic deformation mechanisms. The current state-of-the-art for characterizing thermally-activated dislocation mechanisms consist of measuring activation volume (using transient tests), along with separate *in situ* TEM observations to provide hints about the actual mechanisms. In this work, we take advantage of recent advances in quantitative *in situ* TEM nanomechanics to simultaneously measure activation volume and perform *in situ* TEM observations of the governing mechanisms. This talk will demonstrate the use of a MEMS device to measure true activation volume based on repeated stress relaxation experiments performed inside the TEM. The technique is demonstrated on 100-nm-thick Au and 200-nm-thick Al micro-specimens, providing true activation volume values of 5 and 10 b<sup>3</sup>, respectively. These values will be interpreted in light of the TEM observations performed during these experiments, highlighting mechanisms dominated by grain boundary – dislocation interactions.

#### 2:20pm H2-2-MoA-3 In-situ Microscale Mechanical Testing of Metal/Ceramic Interfacial Regions, X Zhang, Y Mu, S Shao, Wen Jin Meng, Louisiana State University, USA

Application of ceramic coatings onto substrates is an important means of tuning the near-surface mechanical, chemical, and tribological properties of machining tools and mechanical components for improved performance and durability. Successful application of coatings demands adequate interfacial mechanical integrity [1]. Effective engineering of the coating/substrate interfacial region is predicated on establishing experimental protocols for quantitative measurement of interfacial mechanical response and understanding key mechanisms governing interfacial mechanical failure.

We will summarize our results on using in-situ microscale mechanical testing for quantitatively assessing mechanical integrity of metal/ceramic interfacial regions under shear, compression, and tension loading. Quantitative mechanical testing of interfacial regions was accomplished through in-situ SEM instrumented compression and tension loading of focused ion beam fabricated micro-pillars, in which metal/ceramic interfacial regions are placed at various inclinations with respect to the pillar axis [2,3,4]. Such testing, in combination with in-situ SEM observations and detailed post-mortem characterizations, provides new data and new insights on interfacial mechanical failures under different loading conditions. Accompanying simulations, combining density functional theory, molecular dynamics, and crystal plasticity finite element,

provide additional mechanistic interpretations for observed interfacial failures [5,6]. Results of testing on metal/ceramic epitaxial interfaces will also be discussed.

#### References:

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- [2] K. Chen, Y. Mu, W.J. Meng, A new experimental approach for evaluating the mechanical integrity of interfaces between hard coatings and substrates, *MRS Comm.* 4, 19-23 (2014).
- [3] Y. Mu, J.W. Hutchinson, W.J. Meng, Micro-pillar measurements of plasticity in confined Cu thin films, *Extreme Mech. Lett.* 1, 62-69 (2014).
- [4] Y. Mu, X. Zhang, J.W. Hutchinson, W.J. Meng, Measuring critical stress for shear failure of interfacial regions in coating/interlayer/substrate systems through a micro-pillar testing protocol, *J. Mater. Res.* 32, 1421-1431 (2017).
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- [6] X. Zhang., Y. Mu, M. Dodaran, S. Shao, D. Moldovan, W.J. Meng, Mechanical failure of CrN/Cu/CrN interfacial regions under tensile loading, *Acta Mater.*, doi.org/10.1016/j.actamat.2018.08.046 (2018).

#### 2:40pm H2-2-MoA-4 Nano-wedging: A Novel Test Method to Combine Nanoscale Strain Mapping with Multiaxial Stress States, Thomas Edwards, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; F Di Gioacchino, J Pürstl, University of Cambridge, UK; X Maeder, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland; W Clegg, University of Cambridge, UK; J Michler, Empa - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

A novel small-scale mechanical test geometry is presented, which enables a multi-axial stress state to be generated and the deformation characterised in-situ by two non-destructive strain mapping techniques – digital image correlation (nDIC) of a nanoscale Pt speckle pattern e-beam deposited on the side surface of testpieces, and high resolution electron backscatter diffraction (HR-EBSD). To date, such strain mapping methods have only been applied to small-scale mechanical test geometries where the stress state is nominally uniaxial – micropillars, microcantilevers – or at crack tips. By indenting a vertical wall, supported at both ends, with a wedge-shaped indenter, a stress state can be generated which is similar to that produced by standard surface indentation techniques. This method hence gives insight into the evolution of plastic and elastic strains throughout the depth of the material as indentation progresses, in the loaded or unloaded state. Finite element modelling of the test geometry has enabled the nominal stress distribution to be assessed.

This experimental method has been applied to several pure metals – f.c.c., b.c.c and h.c.p – to investigate the evolution of slip band spacing as a function of indentation depth and local plastic strain. It has also been used on MAX phases investigated as novel coating materials for zirconium-based nuclear reactor fuel rod cladding alloys, where certain deformation mechanisms in the MAX phases are not activated in simple uniaxial straining test geometries.

#### 3:00pm H2-2-MoA-5 Micromechanical Characterisation of Ag/Au Multilayers by Means of Bulge and Nanoindentation Testing, Sebastian Krauß, M Göken, B Merle, Friedrich Alexander-University Erlangen-Nürnberg (FAU), Germany

The mechanical properties of metallic thin films are of paramount importance for the performance and reliability of MEMS devices. An approach to further improve the mechanical properties is to introduce a multilayered structure of alternating materials. Therefore metallic Ag/Au multilayered thin film systems were fabricated by thermal evaporation. The overall thickness of the thin film stacks was kept constant to 800 nm, whereas the number of layers in the film and therefore the individual layer thickness were modified. Multilayered systems containing two to sixteen layers were created, resulting in individual layer thicknesses ranging from 400 nm to 50 nm. The microstructure and morphology of the thin films were investigated by atomic force microscopy (AFM) and by cross-sectioning with a focused ion beam system (FIB). The mechanical properties of the thin films were investigated by nanoindentation on glass substrates and by bulge testing of released membranes. The investigations include hardness, yield stress and fracture toughness analysis and are correlated to the microstructure produced by the evaporation process.

# Monday Afternoon, May 20, 2019

3:20pm **H2-2-MoA-6 Size Effect on Superplastic Flow – In situ Micromechanical Characterization of Superplastic Zn-22% Al**, *Patrick Feldner*, M Göken, University Erlangen-Nürnberg, Germany; *B Merle*, Friedrich Alexander-University Erlangen-Nürnberg (FAU), Germany

Superplastic micro & nanoforming has a great potential for a high throughput production of small-scale structural devices with complex geometries. However, it has not yet been established if the macroscopically observed superplastic behavior also persists at microscopic length scales and which fundamental processes govern structural superplasticity in metallic alloys.

For this reason, the micro & nanomechanical properties of the superplastic alloy Zn-22% Al were characterized as a function of the specimen size, using different, complementary in situ micromechanical testing techniques, including micropillar compression in a scanning electron microscope as well as in a X-ray microscope and tensile testing in a transmission electron microscope.

The resulting deformation kinetics clearly reveal a superplastic trend even at the micro scale. However, below a critical specimen volume a breakdown of the superplastic flow behavior is revealed, which is associated with a loss of ductility. Based on the intra as well as intercrystalline deformation morphology observed during in situ testing, this change of the rate-controlling deformation process is discussed in terms of a transition from boundary mediated ductility to boundary mediated brittleness.

3:40pm **H2-2-MoA-7 Studies on the Mechanisms in Hexagonal Close Packed Metal Nanolaminates**, *Irene Beyerlein*, University of California, Santa Barbara, USA

**INVITED**

The goal of this study is to better understand the mechanisms underlying the mechanical response of nanolayered composites containing either pseudo-morphic body center cubic (BCC) Mg or hexagonal close packed (HCP) Mg phases. Nanolayered composites comprised of 50% volume fraction of Mg and Nb were synthesized using physical vapor deposition with individual layer thicknesses  $h$  ranging from 2.5 nm to 50 nm. At the lower layer thicknesses of  $h < 5$  nm the Mg phase was found to have undergone a phase transition from HCP to BCC, such that it formed a coherent interface with the adjoining Nb phase. Hardness testing and micropillar compression testing normal, 45 degrees, and parallel to the interface plane showed that the BCC Mg composite is much stronger and can sustain higher strains to failure. A multiscale, crystal plasticity model incorporating a confined layer slip model for  $h$ -dependent critical resolved shear stresses was developed and applied to understand the linkage between the observed deformation response and underlying mechanisms. Calculations from the model predict that the more homogeneous deformation and reduced plastic anisotropy of the bcc Mg/Nb material compared to the hcpMg/Nb results from dislocation-mediated plasticity on the  $\{110\}$  and  $\{112\}$  slip systems in the Mg phase. The hcp Mg/Nb phase exhibits significant plastic anisotropy due to large differences among the slip strengths of the three HCP slip systems.

4:20pm **H2-2-MoA-9 Critical Assessment of the Criteria for Minimum Indentation Spacing**, *S Pardhasaradhi*, ARCI, India; *Warren Oliver*, KLA-Tencor, USA

With the advances in nanoindentation measurement instrumentation and the associated testing methodologies, high speed indentation mapping with indents that take less than a second to perform, is now possible. This enables mapping large areas with thousands of indents within a few hours which is extremely useful to measure the local mechanical properties of multi-phase alloys, coatings and small volumes of materials. The combination of high-speed mapping techniques and the continuous push towards understanding the mechanical properties of small volumes of materials, has now put greater emphasis on the minimum spacing of indents. In this work, a critical assessment of the minimum spacing of indents is performed, by a combination of extensive indentation experiments ( $\sim 50000$ ) and finite element simulations at different spacings for a wide range of materials including bulk materials and coatings. It was found that a minimum indent spacing of 10 times the indentation depth is sufficient to obtain accurate results for a Berkovich indenter. This is less than half of the commonly followed criteria of spacing the indents three times the size of the indent, which for a Berkovich indent, is approximately 20 times the indent depth. Similar results were also found for other indenter geometries. Finite element simulations are carried out to visualize the plastic zone beneath the indents and to rationalize the experimental findings. It was found that non-overlapping plastic zones is not a requirement for determining the minimum indent spacing and the

observed minimum spacing criteria can be rationalized by simple indentation energy arguments. These results were also found to be applicable for a gold film on a glass substrate, which is an extreme case of soft film on hard substrate that shows significant pile-up. These results have significant ramifications for indentation mapping wherein the indents can now be placed much closer than what was traditionally accepted which enables high resolution mechanical property mapping.

4:40pm **H2-2-MoA-10 Surface Laboratory Assistant – The New Combination of Measurement Device and Analysis Software**, *Nick Bierwisch*, *N Schwarzer*, SIO, Germany

Nowadays the used materials or material combinations in all application fields (e.g. optical, avionic or automotive industry) are getting more and more complex. These complex structures are needed in order to increase the performance and lifetime of the components. Such improvements of each part of your complex device, tool or structural element are necessary to reach the performance goals demanded by the desired application. This increased complexity demands extended analysis and optimization methods. Classical engineering methods and rules of thumb aren't enough anymore.

Proper characterization and optimization of such structures requires invertable mathematical tools of sufficient holistic character. Unfortunately, as such tools are often unavailable trial and error or half empirical sensitivity analysis methods in combination with FEM or BEM are applied. Thereby faster tools could help significantly to save development time and costs [1].

All models (FEM or analytical based) will need exact and generic material parameters for each part of the material system.

SIO [2] has developed several software modules to determine these parameters from different measurement types and created a variety of easy to use software packages which combine these modules.

There are many different measurement devices, where the results could – in principle – be wonderfully combined and successively be applied to obtain a very holistic picture of the strength and weaknesses of a piece of material one is interested in. Only problem there: So far there was no proper joint sewing all these tests and the results they produce seamlessly together.

This unsatisfying situation has changed now.

The talk will demonstrate how the so-called “Surface-Laboratory-Assistant” automatically not only combines various tests, but also improves them, makes suggestions for the next – higher level – test and even automatically starts and subsequently analyses it.

This way and just by the press of a button and in one go, you could get a most comprehensive and sophisticated holistic material analysis from a simple indentation test, via physical scratch up to complex and application orientated tribo-tests.

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

Room Pacific Salon 1 - Session H1-1-TuM

### Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces I

**Moderators:** Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

8:20am **H1-1-TuM-2 Evolution of the Nanoporous Structure of Sintered Ag Joints at High Temperature using In-Situ X-ray Nanotomography**, *Xavier Milhet, A Nait-Ali, D Tandiang, L Signor*, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; *M Legros*, Cemes - Cnrs, France; *Y Liu, D Van Campen*, Stanford Synchrotron Radiation Lightsource - SLAC National Accelerator Laboratory, USA

Silver pastes sintering is a potential candidate for die bonding in power electronic modules. The thin Ag joints, obtained by sintering, exhibit a significant pore fraction thus reducing the density of the material compared to bulk silver. This was shown to alter drastically the mechanical properties (Young's modulus, yield strength and ultimate tensile stress) at room temperature. However, while careful analysis of the nanoporous structure has been reported in 2D, little is known about its quantitative spatial evolution during thermal aging and more specifically during temperature jumps. In this context, high temperature evolutions of the 3D nanoporous structure were observed in-situ using a heater fitted into the beamline 6-2C of SSRL. Segmentation of the porosity and subsequent statistical analysis of the tomographic dataset reveal pore shape, size and spatial distributions evolution during continuous heating. Such an analysis provides insight into the microstructural evolution of sintered nanoporous Ag joints in-service.

8:40am **H1-1-TuM-3 Atom Probe Tomography to Help Understand Deformation Mechanisms in Metallic Alloys**, *Baptiste Gault*, Max-Planck Institute for Iron Research, Düsseldorf, Germany; *P Kontis, S Makineni, J He, Z Peng*, Max-Planck Institut für Eisenforschung, Germany; *S Neumeier*, Friedrich Alexander-University Erlangen-Nürnberg (FAU), Germany; *J Cormier*, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; *D Raabe*, Max-Planck Institut für Eisenforschung, Germany **INVITED**

Atom probe tomography (APT) is a burgeoning materials characterization technique that enables elemental mapping in three-dimensions at the nanoscale and with high elemental sensitivity. APT exploits the effect of an intense electrostatic field to cause the departure of individual atoms, in the form of ions, from the end of a very sharp needle-specimen. The very particular geometry of the specimen gives rise to a highly magnified image formed by the projected ions that are accelerated away from the specimen's surface by the electric field itself. This projection microscope is then coupled with a time-of-flight mass spectrometer to reveal the elemental identity of each of the detected ions. In this presentation, I will cover some of the basics of the technique, I will be showcasing some applications to investigate segregation phenomena induced by the plastic deformation of high-temperature alloys.

9:20am **H1-1-TuM-5 On the Chemical Composition of TiAlN Thin Films - Comparison of Ion Beam Analysis and Laser-assisted Atom Probe Tomography with Varying Laser Pulse Energy**, *Marcus Hans, J Schneider*, RWTH Aachen University, Germany

We compare the chemical composition of TiAlN thin films determined by ion beam analysis and laser-assisted atom probe tomography (APT). The laser pulse energy during APT was increased subsequently from 10 to 20, 30, 40, 50, 100 and 200 pJ within a single measurement, covering the range that is typically employed for the analysis of transition metal nitrides. The laser pulse energy-dependent Ti, Al and N concentrations were compared to ion beam analysis data, combining Rutherford backscattering spectrometry and elastic recoil detection analysis with the total measurement uncertainty of 2.5% relative deviation. It can be learned that the absolute N concentration from APT is underestimated by at least 9% and the absolute Al concentration from APT is overestimated by at least 16%, while absolute Ti concentration values are for both techniques in good agreement. The here presented comparative analysis clearly shows that absolute Al and N concentration values obtained by ion beam analysis deviate significantly to the APT data for the laser pulse energy range from 10 to 200 pJ.

9:40am **H1-1-TuM-6 Microstructure and Oxidation States of Ni in Sub-Nanometric Layer Depending on its Seed-Layer (Zinc Oxide, Silver Layers): A Multi-Techniques Approach to Trespass Limits of Resolution**, *Justine Vorankoff, H Montigaud*, Saint-Gobain Recherche/CNRS, France; *L Largeau*, CNRS/C2N, France; *S Grachev*, Saint-Gobain Recherche/CNRS, France

Functional glazing for thermal isolation consist of stack of layers deposited by PVD magnetron sputtering on flat glass substrates at room temperature. They combine metallic and dielectric thin layers in order to optimize reflectance in the IRs and transmission in the visible. The determination of layers microstructures and chemical states is of great interest for industrials to understand the macroscopic (optical, mechanical) properties of such stacks. Literature is restricted and suffers a lack of adapted techniques. Hence, this is of major interest to develop tools to understand those stacks microstructures.

For this study, we have focused our works on the behavior of ultra-thin layers of nickel or nichrome (< 1 nm) deposited on silver (10-20nm) and zinc oxide layers (5-20nm), which could be found in such functional stacks. First part is dedicated to investigations on the seed layer (ZnO and Ag) which are polycrystalline. AFM images and GIXRD in coplanar and non-coplanar modest to reach key parameters such as crystal size, density of grain boundaries and surface morphology which drastically influences the NiCr layer characteristics. In addition to the heterogeneous environment and the small thicknesses, the oxidation state of Ni and Cr itself impact the layer morphology, which make it challenging to characterize. In order to characterize the NiCr layer depending on the sputtering deposition conditions and its under-layers as best as possible, we use a multi-approach using combined high resolution techniques: AFM, GIXRD, XPS in situ, TEM and STEM-HAADF, Atom Probe Tomography. We use a XPS directly connected to the deposition chamber that enables following the growth at the first stages of the NiCr layer along the deposition process. Using a tilted XPS mode could give us information regarding the growth of NiCr (island or homogeneous layer) without any contact to the atmosphere. Moreover, XPS analysis gives access to the oxidation states of the different species in presence (Ni, Cr and the topmost part of the seed-layer). Coupled with ex situ STEM-HAADF it permits a 2D characterization of crystallites size and distributions, Ni coverage and microstructure depending on the different substrates (Ag, ZnO) and to have chemical information. ATP first results complete those revealed by STEM with the 3D distribution of the species with a sensibility much higher than EDS. All those techniques give complementary information with more or less advantages at different resolutions, which would be discuss and justify their combined use. Deposition conditions for the sputtered layers will be compared as they directly determine the properties discussed above.

10:00am **H1-1-TuM-7 Nanomechanical Investigation on Lateral fcc-w Phase Fields of a Partially Decomposed and Transformed Nano-lamellar CVD fcc-Ti<sub>0.2</sub>Al<sub>0.8</sub>N Coating**, *Michael Tkadletz, A Lechner, N Schallk*, Montanuniversität Leoben, Austria; *B Sartory*, Materials Center Leoben Forschung GmbH (MCL), Austria; *C Mitterer*, Montanuniversität Leoben, Austria; *C Czettl*, CERATIZIT Austria GmbH, Austria

In metastable, nano-lamellar chemical vapor deposited (CVD) fcc-Ti<sub>1-x</sub>Al<sub>x</sub>N coatings, at elevated temperatures, intact fcc-TiAlN areas co-existing with non-lamellar fully decomposed and transformed fcc-Ti(Al)N and w-Al(Ti)N areas could be observed. It is assumed that the observed phase fields and their microstructure strongly correlate with their mechanical properties. To study this correlation, this work focuses on the investigation of a nano-lamellar CVD fcc-Ti<sub>0.2</sub>Al<sub>0.8</sub>N coating in an intermediate sample state annealed at 1050 °C for 5 min, exhibiting fcc- and w-phase fractions side by side. A cross-section of the coating was characterized by means of scanning electron microscopy (SEM) and electron backscatter diffraction (EBSD) measurements and subsequently used for nanomechanical testing. Modulus mappings were performed by evaluating the elastic response after superimposing a dynamically oscillating load to the contact force applied during scanning probe microscopy imaging. Arrays of low load quasistatic indentations on the respective positions provided the basis to create maps of the lateral hardness distribution with a resolution of ~100-200 nm. A cross-correlation of the results with SEM images and EBSD inverse pole figure maps allowed to clearly identify the lateral phase fields and their effects on the mechanical properties. Obtained moduli and hardness values were in good agreement with values measured on the as-deposited and fully decomposed/transformed state. The results of this study clearly demonstrate the power of correlative characterization techniques for the investigation of advanced hard coating materials at the nanoscale.

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

Room Pacific Salon 1 - Session H1-2-TuA

### Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

**Moderators:** Grégory Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

#### 1:40pm H1-2-TuA-1 Complex Study of Thermally Induced Order Reactions in Cu-Au Thin Films, Alla Sologubenko, M Volpi, P Okle, R Spolenak, ETH Zürich, Switzerland

The development of thermally and structurally stable Cu- and Au- based thin films or nano-modulated materials for modern electronic and catalytic applications is the main goal of our work. In our study we follow an effect of thermal treatment on microstructure evolution in Cu-X at.% Au thin films sputter-deposited on rigid and viscoelastic substrates. Complex characterization of thermally induced changes of the material microstructure was carried out by a combination of techniques, transmission electron microscopy (TEM), including time-resolved in-situ heating TEM, and reflectance anisotropy spectroscopy (RAS). While TEM is a well-established technique for phase analyses of nano-dimensional objects, RAS is hardly known as a tool for the microstructure and phase analyses [1]. The validation of RAS as a technique for phase fingerprinting is an alternative goal of our work. Most simple specimen preparation requirements, a non-destructive nature of the optical set-up, high sensitivity to the microstructure state of the material are very attractive features of RAS. The comparison of the TEM and RAS data sets acquired from the same material confirms the unprecedented phase sensitivity of the optical technique and justifies its employment as a prompt, high quality and throughout, routine material characterization method.

Thermally induced phase reactions in Cu-Au bulk alloys are well studied. However, there is little information reported on phase evolution and microstructure stability against thermal annealing in continuous Cu-Au thin films or dewetted nano-modulated structures. A balance between kinetic rates of phase reactions, grain growth and dewetting is affected by an increase of the interface and strain energy contributions to the Gibbs free energy of the thin film system, which in turn can have an effect on the temperature-composition phase fields and the grain morphology.

Our studies confirmed that phase configurations in Cu-Au thin films of 80 and 200 nm thicknesses, accord with the 350°C section of the Cu-Au binary phase diagram [2]. Both, TEM and RAS revealed the stable solid-solution state of Cu-15 at.% Au films in annealed films. The formation of intermetallic phases in Cu-25 at.% Au and Cu-50 at.% Au films upon 350°C annealing was also detected by both, TEM and RAS, but only RAS could reveal the two-phase state of the annealed Cu-25 at.% Au and Cu-50 at.% Au films. The in-situ heating TEM studies show that the 350°C annealing results in nearly concurrent ordering and grain growth in the films with Au content higher than 15 at.%. The time-resolved in-situ heating TEM studies are performed to estimate kinetic rates of both processes.

#### 2:00pm H1-2-TuA-2 Kinetics Dependence of Microstructure and Stress Evolutions in Polycrystalline Cu Films: Real-time Diagnostics and Atomistic Modelling, Clarisse Furgeaud<sup>1</sup>, C Mastail, A Michel, L Simonot, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France; E Chason, Brown University, USA; G Abadias, Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Thin films are currently used in order to decrease the size and improve performances of integrated components in electronic devices. Sputter-deposition is commonly used for growth of metallization layers. It's well established that microstructure, morphology and residual intrinsic stress are strongly correlated to deposition parameters. By combining *in situ* and real-time diagnostics tools a better understanding of the development of film microstructure and intrinsic stress could be achieved for high-mobility metals [1] highlighting the key role of the early stages of growth in the design of thin films morphology.

However, the interplay between deposition parameters and growth kinetics is unexplored, such as the interdependence between growth rate, pressure, flux interruption/resumption on stress build-up and post-growth-

relaxation kinetics. In this study, we propose a methodology based on three different *in situ* and real-time diagnostics tools: Multiple-beam optical stress sensor (MOSS), electrical resistance and surface differential reflectance spectroscopy (SDRS) implemented during sputter-deposition of a model system Cu thin film. Such methodology allows us to obtain relevant and quantitative information on growth and relaxation kinetics. This study was complemented by a systematic *ex situ* characterization by AFM, XRD, and TEM to relate film morphology and microstructure to deposition parameters used.

Besides this experimental approach, we have addressed the atomistic mechanisms responsible for these kinetic effects by computational modelling. We have developed a versatile kinetic Monte Carlo (kMC) code based on a 3D rigid lattice to mimic as much closely as possible the real sputter-deposition conditions. The originality of this code lies on its ability to capture the energetic deposition conditions intrinsic to the sputtering deposition process. Indeed, energetic species constituting the incoming flux are able to drastically alter (sub-)surface processes, such as adatom diffusion and defect creation, and subsequent morphology, microstructure and stress. Finally, the capability of the code to predict stress caused by the diffusion of adatoms in and out of the grain boundaries will be further examined with the final objective to provide a multiscale, predictive computational tool to study the growth and stress kinetics.

[1] G. Abadias *et al.*, Volmer-Weber growth stages of polycrystalline metal films probed by *in situ* and real time optical diagnostics, *APL*, 107, 183105 (2015)

#### 2:20pm H1-2-TuA-3 Understanding the Crystallization of Amorphous Films with Embedded Seed Crystals using High-resolution STEM Composition and Structural Mapping, Paul Rasmussen, J Rajagopalan, R Berlia, Arizona State University, USA

It has been shown recently [1] that by systematically embedding nanometer sized seed crystals into amorphous thin films, their thermally induced crystallization process and final microstructure (mean grain size, grain aspect ratio, and spatial distribution) can be explicitly controlled. Here, we describe the characterization of the seed crystals and their relation to the final grain size, size dispersion and texture of the crystallized films through a combination of spatially resolved, composition and structural mapping in a scanning transmission electron microscope (STEM). We examined two different films (NiTi and TiAl) with a variety of seed crystals (Ti, Cu, Cr) in this work. First, we used energy dispersive X-ray spectroscopy (STEM-EDXS) to obtain the chemical composition with nanometer scale spatial resolution and identified seed crystals (regions with sharply elevated seed element content) in the films. To complement this information, we used automated crystal orientation mapping (ACOM) via precession electron diffraction to identify amorphous (film matrix) and crystalline regions (seed crystals) as well as the orientation of the seed crystals. The combination of STEM-EDXS and ACOM analysis allowed us to map the size dispersion, areal density and spatial distribution of seed crystals and correlate them with the final microstructure of the crystallized film.

1. R. Sarkar and J. Rajagopalan, "Synthesis of thin films with highly tailored microstructures," *Materials Research Letters* 6, 398-405, 2018

#### 2:40pm H1-2-TuA-4 In-situ Investigation of the Oxidation Behavior of Metastable CVD Ti<sub>1-x</sub>Al<sub>x</sub>N Using Combined Synchrotron XRD and DSC, Christian Saringer, M Tkadletz, Montanuniversität Leoben, Austria; A Stark, Helmholtz Zentrum Geesthacht, Germany; C Czettl, Ceratizit Austria GmbH, Austria; N Schalk, Montanuniversität Leoben, Austria

Although hard protective Ti<sub>1-x</sub>Al<sub>x</sub>N coatings deposited by physical vapor deposition methods are well investigated today, their microstructure and properties when synthesized by chemical vapor deposition (CVD) still offer new and scientifically challenging questions. This is mainly owing to the extraordinary structure of CVD Ti<sub>1-x</sub>Al<sub>x</sub>N coatings, typically consisting of Al-enriched Al(Ti)N and Al-depleted Ti(Al)N epitaxial nanolamellae. Within this work, the oxidation behavior of such a nanolamellar coating has been examined using a combination of *in-situ* analytical methods. The coating investigated was composed of approximately 66 wt.-% Al(Ti)N and 32 wt.-% Ti(Al)N face centered cubic phase fractions as well as small amounts of wurtzitic AlN (< 2 wt.-%) deposited on a TiN baselayer. Differential scanning calorimetry (DSC) and X-ray diffraction (XRD) on a powdered sample were simultaneously performed at the P07 beamline at the synchrotron PETRA III in Hamburg during a continuous annealing cycle from 100 to 1400 °C in ambient atmosphere. Together with the DSC signal a sequential Rietveld refinement of the XRD data allowed to precisely determine the onset temperatures of phase transformations and oxidation reactions along with

<sup>1</sup> Student Award Nominee

the quantitative phase composition at any given temperature. The results showed that while the TiN baselayer already started to rutile at temperatures below 550 °C, the Al-containing phases still retained their chemical stability. For the Ti(Al)N and Al(Ti)N phases the onset of oxidation could be observed at approximately 700 and 850 °C, respectively, evidencing the positive influence of Al on the oxidation resistance of Ti<sub>1-x</sub>Al<sub>x</sub>N based coatings. At 1000 °C, oxidation of the coating to rutile and alumina was completed, however, upon further annealing above 1250 °C rutile and alumina were found to form the ternary oxide Al<sub>2</sub>TiO<sub>5</sub>. The sophisticated combination of *in-situ* DSC and XRD at a synchrotron with subsequent Rietveld analysis is a novel approach for the investigation of the thermal stability of metastable coating systems and the results presented demonstrate the potential power of this method. Additionally, annealing in ambient air of the same CVD Ti<sub>1-x</sub>Al<sub>x</sub>N coating on single crystalline alumina substrates with subsequent microstructural analysis allowed to validate the results provided by the *in-situ* investigation of the powdered sample with the behavior of the solid coating.

**3:00pm H1-2-TuA-5 In-situ X-ray Characterization of Liquid-solid Transition Phase in Small Volume, Mohamed Kbibou, L Barrallier, Mechanics, Surfaces and Materials Processing Laboratory, France; M El Mansori, Arts et Métiers ParisTech d'Aix en Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France; L Heraud, Mechanics, Surfaces and Materials Processing Laboratory, France**

This research paper presents a novel *in-situ* X-ray characterization of microstructure and evolution of residual stress during solidification process in small volume, which involves the occurrence of various mechanisms operating concurrently. This is illustrated by the solidification of binary eutectic alloy Bi58%wt-Sn42%wt using *in-situ* X-ray diffraction cell of laboratory instrument to understand the fundamental physical mechanisms that control the liquid-solid transition phase. The diffraction cell is outfitted with a heater under inert atmosphere, temperature control system, thermal isolation and transparent window making X-ray scattering analysis possible at higher temperature. The experimentally obtained temperature dependence of crystal mesh parameters, phase's percent and residual stress is discussed. A Radial Distribution Function Analysis (RDFA) is given at the melting phase of the alloy to describe the short-range order (SRO) and atomic distribution. Also discussed is the evolution of phase transformations and residual stresses on the surface of alloys from room temperature to melting point. The possibilities of this *in-situ* X-ray characterization method to master interplay between microstructure, solidification process variables and functional properties of compounds are highlighted.

**4:00pm H1-2-TuA-8 Novel Quantitative Thin Film Thickness and Chemical State Analysis X-ray Techniques, Wenbing Yun, B Stripe, S Shesadi, S Lewis, X Yang, R Qiao, S Lau, Sigray, Inc., USA**

X-ray based techniques have long been used for thin film characterization, and commonly known approaches include total fluorescence x-ray spectrometry (TXRF) and grazing incidence x-ray scattering systems. However, these laboratory-based approaches have poor spatial resolution due to the limited brightness of the x-ray sources used. On the other hand, techniques based on synchrotron facilities (large particle accelerators that provide intense beams of x-rays) such as micro x-ray fluorescence and micro x-ray absorption spectroscopy (microXRF and microXAS) can provide powerful, spatially resolved information, including: thickness variation, chemistry (e.g. oxidation state and bond lengths), and compositional variation. Such information can be achieved by rastering a focused, high brilliance x-ray beam at microns-scale resolution across the thin film.

Until now, such capabilities at high, microns-scale resolution have been exclusively available at synchrotron facilities, which have limited accessibility and a competitive application process. Sigray, through patented breakthroughs in x-ray source and x-ray optic technologies, has developed two major systems for spatially resolved thin film studies: the AttoMap microXRF system and the QuantumLeap x-ray absorption spectroscopy system.

Here we present the two breakthrough systems and their recent applications, which both provide non-destructive capabilities and the ability to spatially resolve thin films *in situ*, for instance under high temperature and mechanical strain. The microXRF system has spatial resolution down to microns and sub-Angstrom sensitivities, which has enabled it to map thickness variations of coatings and on the order of angstroms with high repeatability and accuracy. The x-ray absorption spectroscopy (XAS) system provides important chemical information for a given element of interest, such as oxidation state and reactivity, bond

lengths, atomic geometry, and nearest neighbor information (such as atomic type).

We will present recent trace-level results of thin films with ~1% repeatability, such as Ar, Hf, Ni and Ti measurements and standard-less ratios for fast and non-destructive characterization. Moreover, we will also present some recent findings on chemical state analysis using the XAS system for applications including battery electrodes and catalyst layers.

**4:20pm H1-2-TuA-9 Effect of Heat Treatment on Microstructure of Erbia Film on Steel Substrate with Yttria Buffer Layer Fabricated by MOCVD, Kenji Matsuda, M Tanaka, S Lee, University of Toyama, Japan; Y Hishinuma, NIFS, Japan; K Nishimura, T Tsuchiya, University of Toyama, Japan**

Erbia and yttria are the promising materials to realize an advanced breeding blanket system because of good electrical resistivity and effective hydrogen permeation suppression. Erbia thin film fabricated via MOCVD process with the yttria buffer layer was formed on steel (SUS316) substrate before and after thermal cycles to investigate the effect of thermal cycling, and their microstructure was confirmed by electron microscopes (SEM, TEM and STEM) and atomic force microscope (AFM) in the present work.

The surface morphology of samples after thermal cycling has small granular structure than samples before thermal cycling and without yttria buffer layer. According to cross sectional observation by TEM and STEM, erbia and yttria have different columnar structure, while yttria buffer layer did not avoid diffusion of elements from SUS316 substrate to erbia layer. The thermal cycling test had not been affected to the growth direction of erbia and yttria layers, which is mostly cube-cube relationship

**5:00pm H1-2-TuA-11 Study of Volmer-Weber Thin Film Growth Mechanisms by Coupling *in situ* Resistivity, Optical and Mechanical Measurements, Quentin Hérault, S Grachev, I Gozhyk, H Montigaud, Saint-Gobain Recherche/CNRS, France; R Lazzari, Institut des Nano Sciences de Paris - Sorbonne Université, France**

Völmmer-Weber growth mode is characteristic of some materials, such as Ag and Au. Before obtaining a uniform film, this growth mode involves complex steps of growth: island nucleation, island growth, percolation and coalescence. It is still a challenge to study these steps with *ex situ* techniques, especially when thin films are not stable after deposition and oxidation. Indeed, low melting points materials -Ag for example- are very mobile due to their low diffusion energy. *In situ* measurements become important to obtain representative information about growth phenomenon happening during deposition process.

To do so, we decided to develop a homemade *in situ* resistivity measurement setup into our DC magnetron sputtering chamber. Coupled to an existing *in situ* mechanical stress measurement setup, this system provided information about coalescence start (mechanical compressive pick), percolation threshold (resistivity fall) and uniform film (mechanical tensile pick). In parallel, our measurements were compared to optical measurement, providing complementary information about coalescence start.

With this setup and playing on deposition technique (continuous and sequentially interrupted), we measured a more or less delayed percolation threshold. We also measured a change in grain size distribution. In addition, using different deposition conditions (power and pressure) and sublayers, we tuned growth in order to finally propose growth mechanisms during Ag thin film deposition, function of deposition rate and diffusion.

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

### Room Pacific Salon 1 - Session H3-1-WeM

#### Variable Temperature Nanomechanics

**Moderators:** Jeffrey M. Wheeler, ETH Zürich, James Gibson, RWTH Aachen University

8:00am **H3-1-WeM-1 On the Activation of Slip in the Mg-Al-Ca Laves Systems: A Combined Study Using High Temperature Indentation, Micropillar Compression and TEM, James Gibson, C Zehnder, S Sandlöbes, S Korte-Kerzel, RWTH Aachen University, Germany**

The mechanical properties of modern, creep-resistant Mg-Al-Ca alloys are significantly influenced by the properties of the intermetallic skeleton at their grain boundaries. During application, these alloys will be thermally cycled from room- to application-temperatures, therefore it is essential to understand how the properties of these intermetallic components vary over this range.

A combination of nanoindentation, AFM, micropillar compression and TEM have been employed to study the behaviour of the Mg<sub>2</sub>Ca Laves phase between room temperature and 250°C. Statistical analysis of the slip lines around inclusions - confirmed by TEM cross-sections - allow rapid analysis of relative CRSS values, supported by direct measurement in micropillar compression.

We show a constant hardness of ~3.5 GPa from room-temperature to 250°C, revealing that Mg<sub>2</sub>Ca is likely the high-temperature strengthening phase of the parent alloy. The trends in slip-plane activation frequency and CRSS with temperature are analysed to explain the overall measurements of hardness.

8:20am **H3-1-WeM-2 Recent Evolution of Instrumentation for Nanoindentation Measurements at Elevated Temperatures, Philippe Kempe, V Haiblíková, Anton Paar, Switzerland**

Characterization of thin film mechanical properties at elevated temperatures has been of scientific and industrial interests for many years, and Instrumented Indentation Testing (IIT) on PVD coatings is bringing useful information. The major limitations in high temperature measurements have been seen as the thermal drift, signal stability (noise) of instrumentation and oxidation of the surface. A defined setup of instrumentation allows to reduce these factors.

The vacuum nanoindentation system is designed to perform reliable load-displacement measurements over a wide temperature range (up to 800 °C). Vacuum has become an essential part of the instrument in order to prevent sample/tip oxidation at elevated temperatures. Independent tip and sample heating as well as an active thermal management of the system answer to the concern of temperature stability. Nevertheless, different experimental aspects of instrumentation are still investigated. It includes frame compliance, indenter tip calibration and verification, and reference samples. The manufacturing of indenter tips and their stability with temperatures is also discussed.

Recent measurements at high temperatures with system characterization and experimental protocol will be presented.

8:40am **H3-1-WeM-3 High Temperature Mechanical Characterization of Binary Cu-X Alloys Produced by Combinatorial Synthesis, Viswanadh Gowtham Arigela, Max-Planck Institut für Eisenforschung, Germany; T Oellers, A Ludwig, Ruhr Universität Bochum, Germany; C Kirchlechner, G Dehm, Max-Planck Institut für Eisenforschung, Germany**

Due to their excellent electrical properties copper-based material systems form the metallization components of most of the thin-film circuits today. The current trend of ever harsher environments and power densities brings the need of enhanced electrical and mechanical properties. It is of particular interest to develop copper alloys with improved strength, which requires the mechanical characterization of these systems at their service conditions on a micrometer length scale. We have used combinatorial material synthesis approaches to synthesize binary Cu-Ag and Cu-Zr alloys with the aim of enhancing the mechanical properties while preserving the electrical properties. The mechanical properties of the alloys were investigated by fabricating free-standing tensile specimens with photolithography techniques from the thin-film material libraries, which were produced by sputtering. Our approach enables high throughput mechanical characterization of a composition range of Cu-(1-8%) X. The

alloys were tested both in the as deposited and in the annealed state. In addition, mechanical properties were also investigated at elevated temperatures (400°C) by tensile testing with a micro deformation stage with a novel method of temperature measurement. The investigations show a substantial improvement of the thin film strength both at elevated and at room temperature along the compositional gradient and a mild influence on the thin film conductivity. Beside the testing protocol and results we will also discuss the mechanism based origin of this behavior with respect to the thin film microstructure.

9:00am **H3-1-WeM-4 Temperature and Strain-rate Dependence of the Mechanical Behavior of Freestanding Gold Thin Films, Benoit Merle, Friedrich Alexander-University Erlangen-Nürnberg (FAU), Germany**

The plastic deformation of freestanding gold films is shown to strongly depend on the testing temperature and strain-rate. These findings were achieved by both creep and constant strain-rate tensile tests, which were performed on evaporated gold films with columnar microstructure. The creep tests were carried out with an upgraded bulge tester operated between 23°C and 100°C. The measurements evidenced a critical temperature of about 75°C, corresponding to a transition in deformation mechanisms from a dislocation based to grain boundary and diffusion mediated plasticity. The influence of the stress was found to be rather low within the investigated range. Constant strain-rate tests were performed in-situ in a TEM, using a novel method for preparing tensile specimens from evaporated thin films. With decreasing strain-rate, the films exhibited a clear transition from shear-coupled grain boundary migration and grain growth to grain boundary sliding, which resulted in strong changes in strength and ductility.

9:20am **H3-1-WeM-5 In-situ Investigation on Mechanical Properties at the Micrometer Scale in Cryogenic Environment, Seok-Woo Lee, University of Connecticut, USA**

**INVITED**

Due to the significant advances in nanotechnology, a structural material at small length scales is becoming more important to develop mechanically robust small devices such as micro-/nano-electro-mechanical systems (MEMS/NEMS). MEMS and NEMS sensor systems that operate in the presence of high/low temperature, corrosive media and/or high radiation can reduce weight, improve machine reliability, and reduce cost in strategic market sectors such as automotive, avionics, oil well logging, nuclear power, and space exploration. Performance of all these small mechanical devices is directly related to mechanical properties of structural materials at small length scales, which are usually "different" from mechanical properties at bulk scale. In order to design a mechanically reliable small device working under various environments, therefore, it is critical to understand "how sample dimension influence mechanical properties of materials" as well as "how environmental conditions influence small-scale mechanical properties." For the last two decades, small-scale plasticity has been extensively investigated by using micro-mechanical tests, and "Smaller is Stronger" and "Smaller is More Ductile" phenomena were observed in various material systems. As briefly mentioned before, the development of sensors and actuators that operates in harsh environment brings a strong attention in small-scale plasticity community. Therefore, materials research, which combines both "size effects" and "environmental effects", is now regarded as next generation research in the field of materials science.

In this presentation, we are going to introduce our ongoing efforts to develop an in-situ nanomechanical testing system operating in cryogenic environments and describe its potential use for materials science research. Then, we will present several examples showing how temperature influences mechanical behaviors of materials at the micrometer scale. The size effects in body-centered-cubic single crystalline metals in cryogenic environments will be discussed, and the strong temperature dependence of power-law exponent will be explained. The size effects in metallic glassy nanolattices will also be presented. Here, we will discuss how thickness of metallic glass and temperature controls ductile-to-brittle transition in nanolattice structures. Finally, we will introduce our recent discovery of superelasticity in ThCr<sub>2</sub>Si<sub>2</sub>-structured intermetallic compounds, and their strong temperature dependence on their superelastic performance and structural transition will be discussed. Their potential use in cryogenic actuators or superconductivity switches for space exploration will be explained, too.

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

### Room Pacific Salon 1 - Session H3-2-WeA

#### Degradation under Extreme Conditions

**Moderators:** James Gibson, RWTH Aachen University, Jeffrey M. Wheeler, ETH Zürich

2:00pm **H3-2-WeA-1 Application of Micro-cantilever Bending to Probe the Fracture Behavior of Thin Film Interfaces**, *J Kabel, Peter Hosemann*, University of California at Berkeley, USA; *T Koyanagi, Y Katoh*, Oak Ridge National Laboratory, USA

Thin film coatings are proposed as a dual-purpose corrosion barrier and hermetic seal for accident tolerant fuel cladding in light water nuclear reactors (LWR). The bulk cladding structure is a SiC/SiC composite as it exhibits high temperature mechanical properties and superior oxidation kinetics in accident scenarios. However, operational LWR coolant conditions and inherent SiC micro-cracking cause matrix dissolution and fission product release respectively. It has been shown that coating technology can mitigate both challenges. A critical aspect of qualifying these coatings for application is to understand the mechanical stability of the interface. Two coating materials, Cr and CrN, have shown promising corrosion behavior and are the subject of this research. Approximately 45 micro-cantilevers,  $\sim 2\mu\text{m}^2$  cross-section and  $6\mu\text{m}$  length, were fabricated using focused ion beam milling techniques and tested *-in situ* SEM to evaluate the interfacial fracture stress. Ductility was observed in the Cr coating, leading a lower-bound fracture stress  $3.25 \pm 0.23$  GPa. Neutron irradiated SiC/Cr interfaces ( $\sim 0.5\text{dpa}$ -SiC at  $330^\circ\text{C}$ ) also showed ductility and a lower-bound fracture stress  $2.9 \pm 0.21$  GPa. SiC/CrN cantilevers showed brittle failure at  $5.55 \pm 0.46$  GPa. Fracture stress was evaluated via the flexural formula following linear elastic beam mechanics assumptions. FEA modelling was pursued to further quantify the complex stress state at the interface, allowing for improved interpretation of the results. Additionally, micro-beam 3pt-bending is being investigated to extract interfacial fracture toughness.

2:20pm **H3-2-WeA-2 Probing Fatigue Resistance in Multilayer DLC Coatings by Micro-impact: Correlation to Erosion Tests**, *Ben Beake*, Micro Materials Ltd, UK; *T Liskiewicz, S McMaster, A Neville*, University of Leeds, UK

Improving the fatigue resistance of multilayered DLC coatings on hardened steel under the harsh environment of highly loaded repetitive contact is key to increasing their performance in demanding applications, such as in automotive engines.

This has been studied directly by (1) micro-scale rapid impact tests at significantly higher strain rate and energy than in the nano-impact test, enabling the study of coating fatigue with spherical indenters (2) dry erosion testing. Good correlation between micro-impact results and erosion results was found.

Hard multilayered a-C:H and Si:a-C:H coatings were found to be significantly less durable under fatigue loading than a multi-layered WC/C coating. The influence of the coating mechanical properties on these differences is discussed. The results of this study provide further strong evidence that in highly loaded mechanical contact applications requiring a combination of load support and resistance to impact fatigue, the optimum lifetime of coated components may be achieved by designing the coating system to combine these properties rather than by solely aiming to maximise coating hardness as this may be accompanied by brittle fracture and higher wear.

2:40pm **H3-2-WeA-3 Development of an In-Situ Ion Irradiation and Nanomechanics Scanning Electron Microscope**, *Khalid Hattar, N Heckman, S Briggs, C Barr, A Monterrosa, C Chisholm, L Treadwell, B Boyce*, Sandia National Laboratories, USA

Understanding the response of coatings and thin films to harsh and often superimposed extreme environments is important for materials selection and prediction of device performance lifetimes. In order to explore the response of materials in these extreme environments, Sandia National Labs is developing, as part of the Center for Integrated Nanotechnologies (CINT) user facility, an in-situ ion irradiation and nanomechanics scanning electron microscope (SEM). The facility being developed couples a JEOL IT300-HRLV SEM with a HVE 6 MV Tandem accelerator and a 1.2 kV KRI KDC10 gridded ion source. This large-chamber field emission SEM can obtain 1.5 nm

resolution, while supporting large samples and high tilt capabilities. The SEM can be operated at a range of pressures (up to 650 Pa) and temperatures (up to 800 C). In-situ SEM ion irradiation is achieved with a 6 MV tandem with available beam species ranging from 800 keV protons to 100 MeV Au ions. Low energy ions can be introduced directly from the tandem ion sources at 46 keV or from the directly connected 1.2 kV ion source that can implant gaseous species at high flux and at energies ranging from 100 eV to 1.2 keV. There are three options for in-situ SEM nanomechanical testing (MTI Fullham heating-straining stage, Hysitron PI-85 nanoindenter, and the custom-built piezo fatigue tester) that significantly expand the range of mechanical properties that can be explored in the SEM. To aid rapid structure and composition analysis during in-situ experiments, the SEM is being outfitted with high speed CMOS based EBSD and large area SSD EDS system. Finally, to provide automated in-situ SEM experiments, a LabVIEW code is being refined that permits direct communication between the SEM, the accelerators, and the nanomechanical stages. To demonstrate these new capabilities, a range of initial experiments will be highlighted including, but not limited to: in-situ compression of additively manufactured (AM) miniature bear figurines, in-situ SEM fatigue in Pt and Pt-Au tensile bars, and in-situ irradiation degradation of an AM composite resulting from 20 MeV Au.

This work was performed, in part, at the Center for Integrated Nanotechnologies, an Office of Science User Facility operated for the U.S. Department of Energy (DOE) Office of Science. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. DOE's National Nuclear Security Administration under contract DE-NA-0003525.

3:00pm **H3-2-WeA-4 Proton Radiation and He Implantation Effect on Radiation-resistant Zr/Nb Sputtered Multilayer Coatings**, *Tomas Polcar*, Czech Technical University in Prague, Czech Republic; *M Callisti*, University of Cambridge, UK; *S Sen, H Yavas*, Czech Technical University in Prague, Czech Republic; *A Lider*, Tomsk State University, Czech Republic

Nanoscale metallic multilayers (NMMs) represent prospective material resistant to intensive radiation damage. Zr/Nb multilayered coatings with a periodicity ( $L$ ) in the range 6 – 167 nm were prepared by magnetron sputtering and studied by a combination of transmission electron microscopy analyses and nanomechanical measurements to reveal deformation and strengthening mechanisms. We can control the mechanical properties by selected deposition conditions leading to various crystallographic orientation or even amorphous Zr layer, whereas Nb layer was kept identical (crystalline) for all depositions. For  $L > 60$  nm, the strengthening mechanism is well described by the Hall-Petch model, while for  $27 < L < 60$  nm the refined CLS model comes into picture. For  $L < 27$  nm; plastic strain measured across compressed NMMs revealed a strong dependence of actual interface between layers. For selected crystallographic orientation Zr layer experiences a hard-to-soft transition. This transition can be avoided by change of crystallographic orientation of Zr layer. In such case, deformation causes structural transformation of Zr from hcp to bcc. The interfaces obtained by experiments are used as an input for DFT simulations to identify helium diffusion and agglomeration in pristine and radiation-damaged Zr/Nb interfaces. Finally, irradiation experiments will be discussed in detail.

3:20pm **H3-2-WeA-5 Tracking the Temporal Oxidation Behavior in TiN Thin Films by In-situ Resistivity Measurements**, *Bastian Stelzer, X Chen, J Sälker, J Schneider*, RWTH Aachen University, Germany

In order to estimate the expected remaining lifetime and safety of thin film components employed in high temperature applications, knowledge of the progress of oxidation is indispensable. A method to estimate the remaining film thickness by in-situ resistivity measurements during oxidation is introduced. To this end, Van-der-Pauw resistivity measurements were performed during oxidation at temperatures up to  $720^\circ\text{C}$  on high power pulsed magnetron sputtered TiN thin films with dc magnetron sputtered Pt electrodes. Based on correlative ex-situ film morphology, structure and local composition data it is evident that the resistivity changes are caused by oxidation of TiN. Thickness measurements of the remaining TiN film thickness under the oxide layer are in very good agreement with calculated TiN thickness data deduced from in-situ resistivity measurements. Hence, we have demonstrated that the temporal oxidation behavior of TiN thin films can be tracked by time resolved in-situ resistivity measurements.

3:40pm **H3-2-WeA-6 Industrial XRF Coating Thickness Analyzer for Real Time Measurement of Aluminum Deposited on Rolled Steel**, *Jelena Hasikova, A Sokolov, A Pecerskis, A Pone, V Gostilo*, Baltic Scientific Instruments, Latvia

Aluminium coatings, deposited by Physical Vapour deposition on the rolled steel products, are more resistant to corrosion in the atmosphere than Zinc coatings. Real time monitoring of coating thickness is very important for the automatic quality control of coating deposition [1].

The industrial coating thickness analyser consists of XRF measuring head, integrated in the vacuum chamber, and remote electrical control unit, containing embedded microprocessor, spectrometric device, electronic circuits, power supply, etc. The measuring head of the analyzer is designed to generate and detect a secondary XRF line, radiated by the Aluminium coating on steel in vacuum. The measuring head is specially designed in order to protect vacuum in process chamber. It is also protected against overheating.

The industrial coating thickness analyser is integrated in the PVD Pilot Line. Measurement of coating thickness is performed directly in the process vacuum chamber. Cold rolled steel strips of different steel grades are used as substrates for PVD process. The amount of aluminium deposited on the surface of the steel strip is in the range from 1 to 20 g/m<sup>2</sup> on studied samples. Accuracy of thin film thickness measurement shown during pre-acceptance test was less than 10 % relative and precision was less than 5 % relative.

Thickness Analyser is included in the factory automatic control system for the technology processes. All data on current measurements in operating and calibration modes, of the status of all spectrometric equipment, including the state of X-ray tube and detector etc. can be transmitted to the computer of upper (factory) level. Based on real-time information about the thickness of the coating, the process engineer and operator can make the right decision to correct the deposition process.

1. A.Sokolov  
[https://www.mdpi.com/search?authors=Aleksandr%20Sokolov&orcid=], J. Hasikova  
[https://www.mdpi.com/search?authors=Jelena%20Hasikova&orcid=], A. Pecerskis  
[https://www.mdpi.com/search?authors=Aleksej%20Pecerskis&orcid=], V.Gostilo  
[https://www.mdpi.com/search?authors=Vladimir%20Gostilo&orcid=], K.Y.Lee  
[https://www.mdpi.com/search?authors=Ki%20Yong%20Lee&orcid=], H.Jung  
[https://www.mdpi.com/search?authors=Hoobok%20Jung&orcid=], J.H.Lim  
[https://www.mdpi.com/search?authors=Jung%20Hyun%20Lim&orcid=]. Application of Industrial XRF Coating Thickness Analyzer for Phosphate Coating Thickness on Steel. *Coatings* 2018, 8(4), 126.

4:00pm **H3-2-WeA-7 In situ Characterization of Dual Phase Diamond-like Carbon (DLC) at Elevated Temperatures**, *Ming Chen*, ETH Zürich, Switzerland; *C Liu, K Li*, City University of Hong Kong, China; *R Spolenak, J Wheeler*, ETH Zürich, Switzerland

Diamond-like carbon (DLC) is routinely used as protective coatings due to their superior wear and friction resistance. However, DLC film is extremely brittle at ambient temperature because of covalent bonds and also notably degraded at elevated temperatures due to graphitization [1]. In this study, dual phases DLC films, i.e. sp<sup>2</sup> and sp<sup>3</sup> phases, were deposited via closed-field unbalanced magnetron sputtering (CFUBMS) with various bias voltages. The microcompression testing at room temperature has revealed a high yield strength of  $\sim E/11$  (E: elastic modulus) and a large plasticity of  $\sim 70\%$  (engineering strain) [2]. This is attributed to the phase transformation of the bonding from sp<sup>2</sup> to sp<sup>3</sup> under stress, which accommodates plastic strain and densifies the materials. The *in situ* micromechanical tests, e.g. microcompression and cantilever bending, were conducted at the elevated temperature range of 100–300 °C to further study the mechanical properties of DLC films at the detrimental temperature conditions. Raman spectroscopy and electron energy loss spectroscopy (EELS) were both applied to quantitatively determine the effect from the content of sp<sup>2</sup> and sp<sup>3</sup> bonds on the mechanical performance. The microstructures after deformation were inspected using high resolution transmission electron microscopy (HRTEM) to elucidate the relationship of processing-structure-property.

[1] Y. Liu, E. Meletis, Evidence of graphitization of diamond-like carbon films during sliding wear, *Journal of Materials Science* 32(13) (1997) 3491-3495.

[2] C. Liu, Y. Lin, Z. Zhou, K.-Y. Li, Dual phase amorphous carbon ceramic achieves theoretical strength limit and large plasticity, *Carbon* 122 (2017) 276-280.

4:20pm **H3-2-WeA-8 In situ micro-Tensile Testing of TiN Coating: Deformation and Fracture in Relation to Residual Stress**, *Erika Judith Herrera Jimenez*, École Polytechnique de Montréal, Canada; *N Vanderesse*, École de Technologie Supérieure, Canada; *T Schmitt, É Bousser*, École Polytechnique de Montréal, Canada; *P Bocher*, École de Technologie Supérieure, Canada; *L Martinu, J Klemberg-Sapieha*, École Polytechnique de Montréal, Canada

Interface engineering is essential to maintain the performance of protective coatings on metallic substrates during the entire product life. In particular, mechanical and microstructural properties of the coating/substrate system are of great importance in order to minimize material failure and improve durability. Deposition of hard coatings and plasma treatment processes can be used to induce compressive residual stress (RS) on the surface of the substrate and to delay the appearance of cracks and thus the material failure. This work presents a study of the effect of substrate plasma pre-treatment by different methods (ion bombardment, ion implantation, nitriding) on the RS of titanium nitride (TiN) coatings, which subsequently affects fracture behaviour of the coating-substrate system. TiN hard coatings with a hardness of  $\sim 23 \pm 2$  GPa, Young's modulus =  $\sim 250 \pm 20$  GPa were deposited by reactive magnetron sputtering onto Ti-6Al-4V aerospace alloy. Glancing angle X-ray diffraction (GAXRD) was used to assess RS profiles of the different coating/substrate interfaces, aiming to elucidate the effect of coating and plasma treatments processes on the Ti-alloy's RS. Each substrate treatment process affected the TiN coating compressive RS from 1 to 4 GPa. Failure mechanism of the coating/substrate interfaces was investigated through *in situ* micro tensile testing employing two configurations: 1) under a laser scanning confocal microscope for non-continuous test and 2) under a monochrome camera for continuous test using digital image correlation (DIC). The Stress-strain curves were obtained from both configuration tests, and for each coating/substrate interface were investigated the formation and propagation of multiple cracks in the thin hard coating, the crack onset strain (COS), energy release rate, stress intensity factor among others. Ti implantation, Ar bombardment and nitriding plasma treatments induced compressive RS into the substrate surface of the Ti-alloy of  $\sim 900$ ,  $\sim 1250$  and  $\sim 1600$  MPa respectively, with higher RS value the crack onset strain (COS) was delayed, while fracture toughness and energy release rate increased.

4:40pm **H3-2-WeA-9 Small Scale Fracture of Mo<sub>2</sub>BC Coatings**, *Hariprasad Gopalan, R Soler, S Gleich, C Kirchlechner, C Scheu*, Max-Planck Institut für Eisenforschung, Germany; *J Schneider*, RWTH Aachen University, Germany; *G Dehm, V Arigela*, Max-Planck Institut für Eisenforschung, Germany

A density functional theory based approach was used to identify Mo<sub>2</sub>BC as a promising candidate for hard coatings with improved fracture properties. A bipolar pulsed direct current magnetron sputtering system was used to deposit a 3 mm thick film on silicon from room temperature to 630°C. An additional thin film was synthesized on sapphire substrate at 900°C. The microstructure of the coatings characterized by transmission electron microscopy reveals that the degree of crystallinity increased with increasing deposition temperatures. The crystalline films possess a columnar morphology with nanocrystalline dimensions. The micro fracture behavior of the free standing coating was characterized by focused ion beam milled pre-notched microcantilever bending tests performed *in situ* in a scanning electron microscope. All cantilevers fractured after purely elastic loading. The fracture toughness of the coatings showed a weak dependence on the substrate deposition temperatures with a maximum of 5 MPa m<sup>0.5</sup>. Fractography revealed the fracture path was either intergranular or through amorphous regions. Additional nanoindentation based fracture toughness estimates were obtained on the coating substrate system showing substantially higher toughness values. The disagreement between the nanoindentation and microcantilever bending experiments was rationalized in terms of a difference in the residual stress in the films which were characterized by wafer curvature measurements. Microfracture experiments in conjunction with nanoindentation revealed Mo<sub>2</sub>BC coatings are excellent candidates as coating materials with high hardness and respectable fracture toughness confirming density functional theory studies.

5:00pm **H3-2-WeA-10 The Effect of Selected Laser Beam Micromilling Parameters on the Surface Layer Structure of HVOF Sprayed WC-CoCr Coating.** **Aleksander Iwaniak**, Silesian University of Technology, Poland; *L Norymberczyk*, ANGA Uszczelnienia Mechaniczne Sp. z o.o., Poland

This study investigated the effect of laser beam micromilling on the surface layer structure of HVOF sprayed WC-CoCr coating. The carbide layer was HVOF sprayed onto flat test samples made of austenitic stainless steel 1.4571 using the Thermico system and CJS K5.2-N gun. Ultra fine-grained WC-CoCr (84/12/4) powder, particle size 10  $\mu\text{m}$ , was used for coat spraying application. The surfaces of test pieces were ground and polished after spraying. Then surface ablation was carried out by micromilling pre-set rectangular-shaped recesses with a nanosecond MOPA pulsed fiber laser. The experiment was planned using the Taguchi method (L9  $3^3$  orthogonal array). The process parameters examined were: laser power, pulse duration and laser beam scanning speed. Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS), X-ray Diffraction (XRD) phase analysis and 3D profilometry were used to evaluate structural changes. The effect of ablation process parameters (laser work parameters) on the treated coating surface condition, removed layer depth, surface roughness after the ablation process and treated coat phase composition was analysed. It was demonstrated that scanning speed reduction and laser pulse duration increase caused the increase of removed material layer thickness at a single beam pass. It was noted that laser treatment resulted in  $\text{W}_2\text{C}$  carbide formation on the treated WC-CoCr coating surface and molten material accumulated at the edges of the openings bored affecting their shapes and topography.

*Acknowledgement:*

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# Thursday Afternoon Poster Sessions, May 23, 2019

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes

### Room Grand Hall - Session HP-ThP

## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

### HP-ThP-1 Cyclic Tensile Deformation of Freestanding, Nanocrystalline NiTi Films using MEMS Stages, *Paul Rasmussen, R Sarkar, J Rajagopalan*, Arizona State University, USA

Controlling the micro/nanostructure of thin films would enable us to explicitly tailor their mechanical behavior. Here, a new process is described in which thin films can be synthesized with precise microstructural control via systematic deposition of nanometer-sized seed crystals, and subsequent crystallization of amorphous precursor films. Using this process, austenitic NiTi (nitinol) films with submicron grain sizes are synthesized. We then co-fabricated freestanding samples of the films with MEMS testing stages and performed cyclic tensile load-unload experiments. Chromium seeded samples showed a high phase transformation stress ( $> 700$  MPa) during the first cycle, with a further increase in transformation stress during subsequent cycles. Unlike the pseudo-elastic behavior typically observed in microcrystalline nitinol, the film showed a continuous decrease in stress-strain slope during unloading. Preliminary in-situ TEM straining studies suggest that this unusual loading behavior is caused by a combination of reverse phase transformation and reverse plasticity.

### HP-ThP-3 Ion Irradiation Behavior of a Nanocrystalline BCC High-Entropy Alloy, *Y Xiao, H Ma, A Sologubenko, R Spolenak, Jeffrey M. Wheeler*, ETH Zürich, Switzerland

Refractory high-entropy alloys (HEAs) have attracted significant attention due to their superior mechanical properties at elevated temperature, making them potential candidates for structural nuclear materials. However, there is little known about their radiation resistance, particular at harsh environment relevant for fission and fusion applications. Here, strongly textured, columnar and nanometer-size-grain NbMoTaW HEA thin films with and without ion beam assisted deposition (IBAD) are produced. They are irradiated with 4.5 MeV Au ions at 77 K and room temperature with doses up to 1000 displacement per atom at ion-channeling direction. Electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM) are used to characterize the microstructural changes. The examined HEA thin film with IBAD technique exhibits superior microstructural radiation resistance compared to normal deposited HEA and W ones. The radiation resistance can be correlated to mechanical properties via nanoindentation.

### HP-ThP-4 Evaluation of Properties in Steel with Hard Coating under Hydrogen, *Noe Lopez Ferrusquia*, Universidad Politecnica Del Valle De México, México; *M Doñu Ruiz*, Universidad Politecnica del Valle de México, México; *C Torres San Miguel*, Sección de Estudios de Posgrado e Investigación de la Escuela Superior de Ingeniería Mecánica y Eléctrica Unidad Zacatenco, Mexico; *V Cortés Suárez, J Garcia Sanchez*, Universidad Autonoma Metropolitana Azcapotzalco, Mexico; *L Sánchez Fuentes*, Universidad Politecnica del Valle de México, Mexico

In this study, on ASTM A36 steel surface with hardened, at 950 °C for 3, 5 and 7h; through dehydrated paste-pack boriding process. Then, They were investigated, the behavior of the specimen hardened superficially in the microstructure, the hardness, the present XRD phases and characteristics by three point bending. Simultaneously, was investigated the hydrogen permeation effect on the coating formed in the surface of the material and the mechanical characteristics, were evaluated by three point bending and hardness. Obtained a layer sawn with the time and temperatures study; likewise the growth of FeB/Fe<sub>2</sub>B layers. There is a hardness change of the boron coating subjected to hydrogen permeation and without hydrogen permeation for each time and temperature. The three-point test showed changes in properties with the coating formed on the surface of the study material subjected to hydrogen permeation and without hydrogen permeation. Showing that the coating boron an efficient alternative to lessen the effect by hydrogen permeation.

### HP-ThP-6 Coatings and Interfaces Characterization: Depth Profiling from the First Nanometer down to the Substrate using RF GD-OES, *Philippe Hunault*, HORIBA Instruments, USA; *M Chausseau, K Savadkouei*, HORIBA Scientific, USA; *P Chapon, S Gaiaschi*, HORIBA Scientific, France

With its capability to perform depth profiling on conductive and non-conductive materials with a nanometric resolution and to go up to 150 µm deep into the sample within few minutes, GD-OES is an ideal tool to evaluate depth profiles on materials and to study interfaces between layers, diffusion processes or to optimize coatings processes. Many elements can be analyzed simultaneously, including Oxygen, Hydrogen, Deuterium, Carbon, Fluorine, Sulfur, Lithium... GD-OES is a versatile tool to study materials that complements other techniques such as XPS and SIMS. Since recently, GD-OES can also be used for the measurement of layer thickness and odd shape samples can be characterized.

Results obtained on various nm thin and thick coatings will be shown during this presentation: The use of RF GD-OES for the optimization of electroplating processes will be described with depth profiles of coatings on both inorganic and organic substrates and the direct determination of thickness using Differential Interferometry. Some results obtained on non-conductive organic coatings used for Aluminum packaging will be shown as well as how GD-OES can be used for thickness measurement on Zinc coatings with a comparison with cross-sectional SEM data. Other examples will include the use of GD to manage quality issues such as unexpected elements at the coating/steel interface or for hot-rolled pipe production.

### HP-ThP-7 In situ Measurement Setup for DC Magnetron Sputtering Thin Film Deposition, *Quentin Herault, S Grachev, I Gozhyk, H Montigaud*, Saint-Gobain Recherche/CNRS, France; *R Lazzari*, Institut des Nano Sciences de Paris - Sorbonne Université, France

DC magnetron sputtering is a common technique of deposition at the industrial scale. It involves complex phenomenon due to the variety of species involved, such as electron, ions, neutral, etc. Consequently, deposition parameters are the key to improve thin film quality. Among them, sample holder potential, deposition speed, deposition pressure, target-sample distance are generally identified as the most pertinent.

To understand the effect of these parameters, we developed different *in situ* measurements methods in the same chamber used during thin film deposition. Surface temperature, mechanical stress, optical reflectivity and resistivity measurement were chosen as complementary methods. Our *in situ* results, correlated to thin film morphology measured by *ex situ* measurements gave a good overview of the impact of deposition parameters on grain size and deposition steps for example.

We propose here to describe this setup and results obtained in the particular case of silver thin film deposition.

### HP-ThP-8 Preparation and Physical Properties of Multiferroic CaMn<sub>7</sub>O<sub>12</sub> Thin Films, *Yu-Chin Tseng*, National Chiao Tung University, Taiwan; *S Jian*, I-Shou University, Taiwan; *C Lin*, National Tsing Hua University, Taiwan; *J Juang*, National Chiao Tung University, Taiwan

This study is aiming at how to prepare epitaxial CaMn<sub>7</sub>O<sub>12</sub> (CMO) films on various substrates by pulsed laser deposition (PLD). The growth temperature for preparing CMO thin films can be between 600 and 700°C. We have tried a wide range of deposition parameters, for example, varying the oxygen pressure from 0.1 to 8×10<sup>-5</sup> torr and also tried to change the laser energy. When using the parameters of 8×10<sup>-2</sup> torr at the 700°C can successfully grow the CMO on the STO(100) substrates. The XRD results reveal that all of the diffraction peaks can be indexed to belong the CMO phase with no obvious preferred orientation and we further used synchrotron radiation sources for XRD measurements to confirm that the obtained samples are indeed with correct phases. In addition, we used phi scan technique to check the symmetry of our thin films. It is could obtain both the CMO thin film and the STO(100) substrate are displaying very clean 4-fold symmetry and displaces 45° with respect to each other. It is also interesting to note that, although the laser energy appeared to have little effects on the formation of crystalline phase and orientation, the AFM examination does reveal significant differences in the film surface morphologies. It is evident that with smaller laser energy, the grain structure appears to be more square-like and when the laser energy was increased, the film grain morphology became more spherical. The typical magnetic properties of the obtained CMO thin films are shown that the present CMO thin films exhibit two magnetic transitions at ~96K (T<sub>N1</sub>) and ~42 K(T<sub>N2</sub>), respectively that measured by SQUID, which in good agreement with the two antiferromagnetic transitions occurring at T<sub>N1</sub>~90 K and T<sub>N2</sub>~48 K reported previously. The fact that our CMO films shows higher T<sub>N1</sub>

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and lower  $T_{N2}$  is also interesting. Nevertheless, the reason that is most likely to cause this phenomenon at present is that the epitaxial strain introduced during film growth.

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## **HP-ThP-9 SIO X-Ray: View Inside your Material with Contact Experiments, Nick Bierwisch, N Schwarzer, SIO, Germany**

Caused by the increasing complexity of materials, be it as coatings, multi-layers, fiber or particle reinforced structures or other forms of compounds, classical engineering methods, linear material models and rules of thumb aren't enough anymore.

Proper characterization and optimization of such structures requires invertible mathematical tools of sufficient holistic character. Therefore, SIO developed analytical models which can dramatically speed up the analysis and simulation of complex contact situations compared to FEM, BEM or other numerical systems.

Together with sophisticated measurement devices it's now possible to characterize even extremely complex material structures in a still completely generic (physical) manner.

The knowledge gained thereby, almost literary allows a view inside the material without cutting it open. In fact, our noninvasive (partially even non-destructive) X-ray technology, which is to say the combination of suitable material test with sophisticated physical analysis, allows a stunning presentation of the material interior with all field components, be it stresses, strains, energies etc.

This way a much easier and - what is more - almost entertaining method of finding initial failure mechanisms and detect weak material spots came into existence.

## **HP-ThP-11 Glow Discharge Optical Emission Spectroscopy: Advances toward Quantitative Coating Compositional Depth Profiling, Amir Tavakoli, F Li, Air Liquide - Balazs NanoAnalysis Laboratory, USA**

As of key analytical data for understanding of functional coatings behavior are (i) coating compositional depth profile, (ii) potential chemical interaction of the coating material with the substrate, and (iii) possible impact of processing environment on the coating composition. Glow discharge optical emission spectroscopy (GDOES) is known as a fast elemental analysis technique for qualitative compositional depth profiling and capable of detecting almost all elements at ppm level. Balazs NanoAnalysis Laboratory with many years of R&D efforts on the GDOES methodology development has proven records of semi-quantitative compositional depth profiling for a variety of metal and ceramic coatings in a range of thickness from 10 nm to 50  $\mu\text{m}$ . In this presentation, a systematic GDOES research work on a series of widely used coatings on aluminum alloys with emphasis on anodized coatings is reported. It is shown how major, minor, and trace element concentrations change from the top-coating surface to the substrate, how the surface elemental composition can be affected from the processing conditions, and how the coating composition is influenced by the diffusion of the substrate constituent elements (coating-substrate interdiffusion). In addition, the reliability of the elemental quantification by GDOES measurements are cross checked using the other elemental analysis techniques.

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 Polcar, T: H3-2-WeA-4, 9  
 Pone, A: H3-2-WeA-6, 10  
 Pürstl, J: H2-2-MoA-4, 3

— Q —

Qiao, R: H1-2-TuA-8, 7

— R —

Raabe, D: H1-1-TuM-3, 5  
 Rajagopalan, J: H1-2-TuA-3, 6; HP-ThP-1, 12  
 Rasmussen, P: H1-2-TuA-3, **6**; HP-ThP-1, **12**  
 Rupert, T: H2-1-MoM-5, 1; H2-1-MoM-6, 1

— S —

Sälker, J: H3-2-WeA-5, 9  
 Sánchez Fuentes, L: HP-ThP-4, 12  
 Sandlöbes, S: H3-1-WeM-1, 8  
 Saringer, C: H1-2-TuA-4, 6  
 Sarkar, R: HP-ThP-1, 12  
 Sartory, B: H1-1-TuM-7, 5  
 Savadkouei, K: HP-ThP-6, 12  
 Schalk, N: H1-1-TuM-7, 5; H1-2-TuA-4, 6  
 Scheu, C: H3-2-WeA-9, 10  
 Schmitt, T: H3-2-WeA-8, 10  
 Schneider, J: H1-1-TuM-5, 5; H3-2-WeA-5, 9;  
 H3-2-WeA-9, 10  
 Schuler, J: H2-1-MoM-5, 1  
 Schwarzer, N: H2-2-MoA-10, 4; HP-ThP-9, 13  
 Sebastiani, M: H2-1-MoM-7, 1  
 Sen, S: H3-2-WeA-4, 9

Shao, S: H2-2-MoA-3, 3

Shesadri, S: H1-2-TuA-8, 7

Signor, L: H1-1-TuM-2, 5

Simonot, L: H1-2-TuA-2, 6

Sokolov, A: H3-2-WeA-6, 10

Soler, R: H3-2-WeA-9, 10

Sologubenko, A: H1-2-TuA-1, 6; HP-ThP-3, 12

Spolenak, R: H1-2-TuA-1, 6; H3-2-WeA-7, 10;  
 HP-ThP-3, 12

Stangebye, S: H2-2-MoA-2, 3

Stark, A: H1-2-TuA-4, 6

Stelzer, B: H3-2-WeA-5, 9

Straub, T: H2-1-MoM-3, 1

Stripe, B: H1-2-TuA-8, 7

— T —

Tanaka, M: H1-2-TuA-9, 7  
 Tandiang, D: H1-1-TuM-2, 5  
 Tavakoli, A: HP-ThP-11, **13**  
 Tkadletz, M: H1-1-TuM-7, 5; H1-2-TuA-4, 6  
 Torres San Miguel, C: HP-ThP-4, 12  
 Treadwell, L: H3-2-WeA-3, 9  
 Tseng, Y: HP-ThP-8, **12**  
 Tsuchiya, T: H1-2-TuA-9, 7

— V —

Van Campen, D: H1-1-TuM-2, 5  
 Vanderesse, N: H3-2-WeA-8, 10  
 Volpi, M: H1-2-TuA-1, 6  
 Voronkoff, J: H1-1-TuM-6, 5

— W —

Wardini, J: H2-1-MoM-5, 1  
 Wheeler, J: H3-2-WeA-7, 10; HP-ThP-3, **12**

— X —

Xiao, Y: HP-ThP-3, 12

— Y —

Yang, X: H1-2-TuA-8, 7  
 Yavas, H: H3-2-WeA-4, 9  
 Yun, W: H1-2-TuA-8, 7

— Z —

Zehnder, C: H3-1-WeM-1, 8  
 Zhang, X: H2-2-MoA-3, 3