Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 4-6 - Session H3-1

Characterization of Coatings in Harsh Environments

Moderators: David Armstrong, University of Oxford, Jeff Wheeler, Laboratory for Nanometallurgy, ETH Zürich

8:00am **H3-1-1 Small-Scale Mechanical Testing on Ion Beam Surface-Modified Engineering Materials**, ***Peter Hosemann,*** University of Californa at Berkeley, USA **INVITED**

Ion beam irradiation has been utilized to enhance surface properties of materials but also as a surrogate for neutron irradiation damage which is a truly harsh environment. Due to the limited penetration depth of ion beam irradiation, small scale mechanical testing is required in order to evaluate mechanical properties in the region on interest. In this work we present small scale mechanical test data on ion beam irradiated steels. We will feature nanoindentation, microcompression testing as well as micro tensile testing. We find that while nanoindentation and microcompression testing provides a good measures of hardening and yield strength the tensile testing gives inside into the plasticity. The load drops occurring during the testing are able to provide inside into localized failure and dislocation activity to the point where semi quantitative load drop analysis can be used as a parameters for slip channel formation. In addition a new method of Helium implantation using the ORION Nanofab He ion beam microscope is presented with subsequent mechanical property measurements of the implanted region.

8:40am **H3-1-3 High Temperature Nanoindentation up to 800°C: Experimental Optimization**, *N Randall, M Conte,* Anton Paar TriTec, Switzerland*; J Schwiedrzik, J Michler,* EMPA, Switzerland*;* ***Pierre Morel,*** Anton Paar, USA

One of the primary motivations for development of instrumented indentation was to measure the mechanical properties of thin films. Characterization of thin film mechanical properties as a function of temperature is of immense industrial and scientific interest. The major bottlenecks in high temperature measurements have been thermal drift, signal stability (noise) and oxidation of the surfaces. Thermal drift is a measurement artefact that arises due to thermal expansion/contraction of indenter tip and loading column. This gets superimposed on the mechanical behavior data precluding accurate extraction of mechanical properties of the sample at elevated temperatures. Vacuum is essential to prevent sample/tip oxidation at elevated temperatures.

This talk will summarize the latest design of the UNHT^3 HTV nanoindentation system that can perform reliable load-displacement measurements up to 800°C. The sample, indenter and reference tip are heated separately and the surface temperatures matched to obtain drift rates as low as 1nm/min at 800 °C, without any correction. Particular focus will be placed on recent developments which are of high importance in being able to accurately analyze high temperature nanoindentation data. These include the validation of instrument calibration across the entire temperature range, the determination of indenter area function and modelling of the temperature transfer between the sample surface and the tip, as well as compliance considerations. It is only by solving these issues that truly accurate mechanical properties can be calculated from high temperature load-depth data.

9:00am **H3-1-4 Size-dependent Nanoscale Plasticity in Oxidation-strengthened Zr/Nb Multilayers**, ***Mauro Callisti,*** University of Southampton, UK*; M Monclus,* IMDEA Materials Institute, Spain*; J Llorca,* Polytechnic University of Madrid, Spain*; J Molina-Aldareguía,* IMDEA Materials Institute, Madrid, Spain*; T Polcar,* University of Southampton, UK

Nanoscale metallic multilayers (NMMs) represent a relatively new class of heterogeneous materials often used to understand the relationship between intrinsic materials properties (grain size, interfaces, etc.) and the corresponding mechanical properties. Among the possible combinations, Zr/Nb (*hcp/bcc*) NMMs were investigated in this study, as the strengthening mechanisms and the oxidation behaviour of Zr/Nb NMMs are not understood. Furthermore, Zr-Nb alloys are widely employed in nuclear industry; therefore, in view of the positive role of interfaces against radiation damage, Zr/Nb NMMs could represent a promising candidate material for the future nuclear industry.

In this study, Zr/Nb multilayers with a periodicity (L) ranging between 10 – 75 nm were deposited by magnetron sputtering and subsequently annealed at 350 for different annealing times (2 – 168 hrs). Analytical electron microscopy, *in-situ* XRD and nano-mechanical testing were combined to reveal the oxidation process as well as the deformation mechanisms in pristine and annealed samples.

The oxidation process occurred in a selective way in Zr/Nb NMMs, where Zr rapidly transformed into monoclinic ZrO_2, while Nb progressively oxidised at a much lower rate to form a Nb_2O_5 phase. The sequential oxidation of Zr and Nb layers was key for the oxidation to take place without rupture of the layered structure. Micropillar compression tests revealed that in Zr/Nb NMMs with L = 10 nm the deformation mechanism was mostly governed by shear bands formation in softer non-oxidised regions. Conversely, for larger periodicities (L = 75 nm) the mechanical properties of individual layers played a more dominant role on the deformation mechanism. In particular, in the as-deposited Zr/Nb co-deformation of Zr and Nb occurred, although Nb layers were slightly extruded out between Zr layers. On the other hand, in the annealed Zr/Nb NMMs (L = 75 nm) both Nb and Nb_2O_5 layers were found to control the deformation mechanism.

9:20am **H3-1-5 High Temperature Mechanical Properties Characterization of DLC Films**, *M Rouhani,* National Chung Cheng University, Taiwan*; F Hong,* National Cheng Kung University, Taiwan*;* ***Yeau-Ren Jeng,*** National Chung Cheng University, Taiwan

Thermal stability of various DLC films is an important factor determining their application range. Up to know, all the studies on the thermal stability of DLC films were limited on the annealing of the films at elevated temperature and then characterization of the changes in material structure and properties at room temperature. In this study, we have used special equipment which allows us to do in-situ characterization at elevated temperatures in order to understand materials behaviour close to service conditions. In order to investigate the effect of temperature on the mechanical properties of DLC films, three series of DLC films were successfully deposited on Si substrates using filtered cathodic arc vacuum (FCVA) deposition system. All the deposition parameters for these three series were kept constant; except Ar pressure (P_{Ar}) which varied from 0.5 to 1 and finally to 1.5 mTorr. The hardness and modulus of the films were measured at 21, 40, 60, 80, 100, 120, 140, 180, 200, 250, 300, 350, 400, 450 , 500̊C using a nanoindenter. At room temperature the film deposited at the lowest P_{Ar} (0.5 mTorr) shows the highest hardness (36 GPa), followed by the film deposited at P_{Ar}=1 mTorr with hardness of 26 GPa, while the film deposited at the highest P_{Ar} shows the lowest hardness (18 GPa). The microstructure of the films at room temperature was characterized using Raman spectroscopy and the findings confirm the reduction in sp^3/sp^2 ratio by increasing the P_{Ar} during the deposition process. Increasing the temperature during the hardness measurement, results in hardness reduction of all the films, and at temperatures above the 350̊C some of the films start to delaminate. More interestingly, for annealing temperature lower than 300̊C, when the substrate temperature is returned to room temperature, the hardness of the DLC films rise again close to the hardness values measured originally at room temperature, although small reduction is noticeable which may be due to stress reduction. To investigate the mechanism behind the hardness dependence on the temperature test, several nano-wear tests were carried out at room temperatures and elevated temperatures and we could see changes in worn area and its surroundings using Raman spectroscopy. Overall, our in-situ experiment coupled with annealing tests may explain why previous reports could not see significant reduction in hardness after annealing, while in close to service conditions, the harness of the DLC films significantly reduces at elevated temperature.

9:40am **H3-1-6 Aluminide Coatings on Thin-Walled Sheets – Mechanical Properties and Thermocyclic behaviour**, ***Johannes Bauer,*** DECHEMA-Forschungsinstitut, Germany*; H Ackermann,* Oel-Waerme-Institut, Germany*; M Galetz,* DECHEMA-Forschungsinstitut, Germany

Sheets in industrial furnaces and oil burners are exposed to high temperatures and aggressive atmospheres. For service conditions involving temperatures below 900°C and low mechanical stresses, relatively inexpensive heat-resistant steels are usually used. For higher exposure temperatures, currently cost-intensive Ni-based alloys have to be employed even for low stress applications. Aluminized austenitic steels are a suitable alternative. Under service conditions Al diffuses not only outwards to form the protective α- Al_2O_3 scale, but also inwards to the substrate because of the concentration gradient. Simultaneously, the substrate elements e.g. Fe, Cr and Ni diffuse outwards. As a consequence the thickness and the microstructure of the diffusion zone (DZ), interdiffusion zone (IDZ) and the substrate are altered. In the case of thin-walled components the microstructural evolution of the coated system and the subsequent change of the mechanical properties cannot be neglected and have a strong influence on the lifetime of the system.

In this study, heat-resistant austenitic steels (X15CrNiSi20-12 and X15CrNiSi25-21) were aluminized via pack cementation with coating thicknesses varying between 40-130 µm to enhance their corrosion resistance up to 1000°C. Uncoated samples were investigated for comparison. Thermocyclic exposure tests were performed and the alteration of the microstructure of DZ, IDZ and substrate was analyzed. Furthermore tensile tests at room temperature and creep-rupture tests in burner exhaust atmosphere were conducted to show the influence of the coatings on fundamental mechanical properties.

The results reveal the influence of the coating on the overall mechanical behavior and corrosion resistance of the coated system.

10:00am **H3-1-7 Variable Temperature Micropillar Compression Transient Tests on Nanocrystalline Palladium-Gold: Probing Activation Parameters at the Lower Limit of Crystallinity***, **Juri Aljoscha Wehrs**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The plasticity of nanocrystalline metals is governed by a complex ensemble of deformation mechanisms which strongly depends on the materials grain size. Smaller grains are less effective in generating dislocations and hence their ability to interact across intercrystalline domains is reduced. Therefore it is instructive that, in particular for that case that grain sizes approach the limit of crystallinity towards the amorphous regime, grain boundary-mediated deformation processes gain influence while dislocation-mediated processes fade. Mechanisms which essentially emerge from the core regions of grain boundaries, such as grain boundary sliding, grain boundary migration, dislocation nucleation and shear transformation zones are under debate. Consequently, both thermally activated and inelastic, stress-driven deformation processes can be simultaneously operative in these materials. All of these mechanisms contribute towards the increased time dependent plasticity of nanocrystalline metals, manifesting itself as a high degree of strain-rate sensitivity and susceptibility to load relaxation and creep even at room temperature.

In this study we explore the strain rate sensitivity and the load relaxation properties of a highly pure nanocrystalline $Pd^{90}Au^{10}$ alloy with an extremely fine nominal grain size of d~10nm by means of dynamic micropillar compression experiments at variable temperatures. First we briefly review and discuss the testing technique, our experimental considerations and data analysis methods. Then we focus on the applicability of this type of micromechanical experiment for probing activation parameters in nanocrystalline materials. The extracted activation parameters (i.e. strain rate sensitivity, activation volume and activation energy) are discussed and compared to literature data to gain insights into the possible rate controlling deformation mechanisms at the lower limit of crystallinity.

10:20am **H3-1-8 High Temperature Micro-Mechanical Testing of Aluminide Coatings***, **James Gibson**, H Reuß, J Schneider, S Korte-Kerzel,* RWTH Aachen University, Germany

The effect of thin film composition and temperature on the elastic, plastic and fracture properties of transition metal nitride and oxynitride coatings was invested by nanoindentation, micro-cantilever bending and micro-pillar compression. Vanadium aluminium nitride (VAlN) and vanadium aluminium oxynitride (VAlON) coatings were manufactured by high-power impulse magnetron sputtering on silicon substrates. A focused ion beam was used to cut notched micro-cantilever beams to determine values of fracture toughness and micro-pillars were cut to observe plastic deformation in otherwise brittle coatings. Tests were carried out to 500°C in-situ using a Nanomechanics inSEM system.

A room temperature fracture toughness measurement of 2.3 and 2.6 MPa√m was measured in the VAlN and VAlON, respectively.

10:40am **H3-1-9 Temperature-dependent Interfacial Layer Formation during Sputter-deposition of Zr Thin Films on Al_2O_3(0001)***, **Koichi Tanaka**, J Fankhauser,* University of California, Los Angeles, USA*; M Sato,* Nagoya University, Japan*; D Yu, A Aleman, A Ebnonnasir, C Li,* University of California, Los Angeles, USA*; M Kobashi,* Nagoya University, Japan*; M Goorsky, S Kodambaka,* University of California, Los Angeles, USA

Zirconium thin films are attractive as protective layers in nuclear reactors and in chemical processing plants owing to its mechanical and corrosion-resistant properties. Relatively little is known concerning the growth-related aspects of Zr thin films. Here, we present results from investigation of the effect of substrate temperature (600 °C ≤ T_s ≤ 900 °C) on microstructure of Zr thin films grown on Al_2O_3(0001) via dc magnetron sputtering in an ultra-high vacuum deposition system with base pressure < 5×10^{-10} Torr. ~220-nm-thick Zr films are deposited at a rate of ~0.06 nm/s from Zr target (99.1 wt.% pure with 0.8 wt.% Hf) in 10 mTorr Ar (99.999%) atmosphere. The as-deposited layers are characterized using x-ray diffraction, cross-sectional transmission electron microscopy along with energy dispersive spectroscopy. At 600 °C ≤ T_s ≤ 700 °C, we obtain hexagonal close-packed structured Zr(0001) thin films. At T_s < 750 °C, the layers are dense with smoother surfaces. At T_s ≥ 750 °C, the Zr layers are highly textured with {0001} as the preferred orientation. The films are increasingly porous with highly corrugated surfaces. We find that the Zr/Al_2O_3 interfaces are not abrupt but that there exists an additional layer whose thickness increases with increasing T_s from 10 ± 4 nm at 600 °C to 116 ± 4 nm at 900 °C. These interfacial layers are primarily composed of Zr and Al and their relative concentrations vary with T_s.

Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 4-6 - Session H3-2
Characterization of Coatings in Harsh Environments

Moderators: David Armstrong, University of Oxford, Jeff Wheeler, Laboratory for Nanometallurgy, ETH Zürich

2:10pm **H3-2-3 Recent Advances in Nanomechanical Testing of Thin Films: Variable Temperature, Ultra-high Strain Rates, in-situ EBSD Experiments***, J Best,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wheeler,* Laboratory for Nanometallurgy, Department of Materials Science, ETH Zürich, Switzerland*; J Wehrs, J Schwiedrzik, G Mohanty, J Ast, X Maeder, K Thomas,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Morstein,* Platit Ag, Switzerland*; **Johann Michler**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland **INVITED**

We've developed two recently two platforms for variable temperature nanomechanical testing. The first platform allows for variable temperature and variable strain rate testing of micropillars in situ in the scanning electron microscope. By utilizing an intrinsically displacement-controlled micro-compression setup, which applies displacement using a miniaturized piezo-actuator, we've recently extended the attainable range of strain rates to up to~ 10^4 s^{-1}, and enabled cyclic loading up to 10^7 cycles. Stable, variable temperature indentation/micro-compression in the range of -150°C to 600°C is achieved. Combination with in situ EBSD allows for the determination of crystallographic orientation with sub-100 nm spatial resolution. Thereby, it provides highly localized information on phenomena such as elastic bending of the micropillar or the formation of deformation twins and plastic orientation gradients. A second system allows for measurements at lower loads ex-situ in a dedicated vacuum chamber in the range of -150 °C to 700 °C.

Using these new capabilities, we examine the plasticity and fracture of thin films. Variable strain rate and variable temperature micro-compression experiments on metal multilayers were performed. Activation parameters such as activation energy and activation volume were determined and discussed in view of the most probable deformation mechanism. To study fracture and fatigue behavior of nanocrystalline ceramics thin films several different small-scale fracture toughness geometries were compared and impact testing using a flat punch was performed, respectively. It was found that notching using a focused gallium source influences small-scale toughness measurements and can lead to an overestimation of the fracture toughness values for chromium nitride (CrN) thin films. Impact testing at 500 Hz up to temperatures of 500 °C showed increased CrN plastic behavior at high temperatures, and demonstrated the usefulness of the equipment for performing accurate small-scale impact tests. Finally, during a more measurement method oriented research project, we explored in-situ HR-EBSD to estimate the size of the plastic zone underneath the crack tip during micro-cantilever fracture tests in tungsten single crystal. We demonstrate the mapping of the evolution of the stress field around the notch tip and the estimation of the GND density in the plastically deformed zone.

2:50pm **H3-2-5 Combined Size and Texture-dependent Deformation and Strengthening Mechanisms in Zr/Nb Nano-multilayers in Harsh Environments***, **Tomas Polcar**, M Callisti,* University of Southampton, UK

A combination of transmission electron microscopy analyses and nanomechanical measurements was performed to reveal deformation and strengthening mechanisms occurring in sputtered Zr/Nb nanoscale metallic multilayers (NMMs) with a periodicity (*L*) in the range 6 – 167 nm. Electron diffraction analyses revealed a change in the crystallographic orientation of α-Zr when *L* 27 nm, while Nb structure retained the same orientations regardless of *L*. 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. A decrease in strength is found for $L < 27$ nm, which could not be simply explained by considering only misfit and Koehler stresses. For *L* 27 nm, plastic strain measured across compressed NMMs revealed a change in the plastic behaviour of α-Zr, which experienced a hard-to-soft transition. Further decrease in L led to crystallographic orientation change of α-Zr with a consequent change of the dominant slip system. The actual strength at these smaller length scales was effectively quantified by taking these structural aspects into account in the interface barrier strength model. Then the multilayers were subject to irradiation (gamma) and high energy implantation (He, C, Si, Cu) and the effects of radiation damage on mechanical properties were studied in detail.

3:10pm **H3-2-6 The Oxidation Resistance of ZrO_2-Coated and Vacuum Annealed ZrN-Coated Zircaloy-4***, **I-Sheng Ting**, J Huang, G Yu,* National Tsing Hua University, Taiwan

The purposes of this study were to evaluate the oxidation resistance of ZrO_2-coated Zircaloy-4 (Zry-4) and investigate the effect of vacuum heat treatment on ZrN-coated Zry-4. Oxidation is a crucial problem for the Zry-4 fuel cladding of light water nuclear reactor. Ceramic coatings, such as CrN, SiC, and Si_3N_4 have been proposed for increasing the corrosion resistance of Zry-4. In general, when reacting with water, Zry-4 will spontaneously form a surface oxide layer that is composed of both tetragonal and monoclinic ZrO_2. Nevertheless, the oxide layer is only several nanometers, which is insufficient to protect the substrate from the severe environment in reactor. Therefore, this study aimed to compare the oxidation resistance between directly deposited ZrO_2 thin film about 500 nm on Zry-4 using unbalanced magnetron sputtering (UBMS) and those formed by vacuum annealed ZrN-coated Zry-4 at 1000 °C for 1 h. After the deposition of ZrO_2 thin films and vacuum annealing of ZrN thin films, X-ray diffraction (XRD) was used to characterize the structure. The residual stresses in the ZrO_2 and annealed ZrN thin films were respectively determined using $\cos^2\alpha\sin^2\psi$ XRD method. Our preliminary study showed that the contact angle of ZrN thin film on Zr metal is about 50° and that of ZrO_2 thin film on AISI 304 stainless steel is roughly 86°. Both results indicated high contact angles between the coatings and substrates, which accounting for adhesion problems. It was also found that the poor wettability between ZrO_2 and AISI 304 stainless steel even resulted in poor corrosion resistance. Therefore, the wettability of ZrO_2 on Zry-4 and ZrN on Zry-4 was evaluated in this study through contact angle tests. Thermogravimetric analyzer (TGA) and focused ion beam (FIB/SEM) were used to characterize the oxidation behavior and observe the oxide thickness, respectively. The compositional depth profiles were determined by Auger electron spectroscopy (AES). Based on the experimental results, the feasibility of the oxidation protective coatings was evaluated.

3:30pm **H3-2-7 Effect of Using Dissimilar Substrate Materials on Interfacial Properties of HVOF Deposited Inconel 718 Alloy***, **Sahar Abualigaledari**, M Salimijazi, F Azarmi, Y Huang,* North Dakota State University, USA

Coating and substrate interfacial properties highly influence the characteristics and performance of the entire coating system. Thus, it has been a primary concern especially in the case of repairing components using thermal spraying process. Due to the nature of thermal spraying deposition, it is speculated that stronger interface will form in the case of similarity between substrate and coating material. This work is an attempt to evaluate the bonding strength of the thermal spray coatings deposited on similar and dissimilar substrate materials. To this end, Inconel 718 was deposited on Inconel 718 and Steel substrates using High Velocity Oxygen Fuel (HVOF) technique. Microstructural characteristics, phase, and elemental distribution of the coatings were studied by Scanning Electron Microscopy (SEM), Electron Dispersive Spectroscopy (EDS), and X-ray Diffraction (XRD). Vickers indentation technique and lap shear test were employed to investigate the mechanical properties of coating-substrate interface and coating layers. The resulted hardness values were applied in an empirical model known as Palmqvist method to assess the fracture toughness and bonding strength of the coatings. Residual stress distribution analysis was also implied across the coatings, using XRD technique, to validate the data. The results indicated better interfacial strength of Inconel 718/Inconel 718 since its shear strength and fracture toughness were higher than that of Inconel 718/Steel sample.

3:50pm **H3-2-8 Sublimation and Self Freezing of Planar Surfaces in Rarefied Atmospheres***, **Rahul Basu**,* Adarsha Institute of Technology, India

A simulation of phase transformations in planar geometries under various boundary conditions is performed. The case of ablation, accretion and self freezing under rarefied atmospheres and application of external heating is looked at for the ice-water-vapor and naphthalene systems. Consideration of ablation is important in applications with space shields in space flight under radiation and heat sources along with near vacuum conditions. Recent Non invasive methods in cryogenic surgery also rely on production of extreme cold in subcutaneous layers by surface ablation. In this paper, sample calculations for water-ice and naphthalene give the velocities of the freezing and vaporization fronts under various parameter combinations, assuming isotropic properties in each phase. It is shown that considerable difference exists between the cases of self freezing, ablation and accretion.

For instance in the case of water, rates of self ablation without heat sources and self accretion (as in the formation of ice crystals directly from vapor) differ by an order of Magnitude

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H2-1

Advanced Mechanical Testing of Surfaces and Coatings

Moderators: Benoit Merle, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Marco Sebastiani, University of Rome "Roma Tre"

8:00am **H2-1-1 Controlling Disorder in Vapor-deposited Metallic Thin Films and its Influence on Mechanical Behavior**, *D Magagnosc,* University of Pennsylvania, USA*; G Balbus,* University of California Santa Barbara, USA*; G Feng,* Villanova University, USA*; **Daniel Gianola,*** University of California Santa Barbara, USA **INVITED**

The nonequilibrium nature of kinetically frozen solids such as metallic glasses (MGs) is at once responsible for their unusual properties, complex and cooperative deformation mechanisms, and their ability to explore various metastable states in the rugged potential energy landscape. These features coupled with the presence of a glass transition temperature, above which the solid flows like a supercooled liquid, open the door to thermoplastic forming operations at low thermal budget as well as thermomechanical treatments that can either age (structurally relax) or rejuvenate the glass. Thus, glasses can exist in various structural states depending on their synthesis method and thermomechanical history. Despite the ability to make MGs in bulk form (cm-size or larger) and their appealing properties, the full spectrum of structural states in MGs and the corresponding mechanical behavior is relatively unknown, stymying the tuning of MG properties via informed processing and synthesis routes. Recent reports of organic glasses synthesized by physical vapor deposition show a degree of control not available in bulk materials and the occurrence of ultrahigh kinetic stability – so-called ultrastable glass formation.

Here, we use sputter deposition while varying the substrate temperature, to isochemically control the structural state and concomitant mechanical response in a Pd-based MG thin film at the time of glass formation. Increasing the deposition temperature from 333 K to 461 K results in a 33.5% increase in hardness to 9.69 GPa for amorphous films. Further increasing the temperature leads to a decrease in hardness, indicating low and high temperature deposition regimes where increased surface mobility allows access to a more relaxed and more rejuvenated structure, respectively. Through this mechanism we access the range of achievable structural states, from ultrastable to highly liquid-like glasses.

8:40am **H2-1-3 Influence of Microstructure on the Cyclic Electro-mechanical Behavior of Ductile Films on Polymer Substrates***, **Megan Cordill,** O Glushko,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences and Monanuniversität Leoben, Austria*; D Többens,* Helmholtz-Zentrum Berlin für Materialien und Energie, Germany*; C Kirchlechner,* Max-Planck-Institut für Eisenforschung GmbH, Germany

In order to advance flexible electronic technologies it is important to study the combined electro-mechanical properties of thin metal films on polymer substrates under mechanical load. Ductile films and lines are an integral part of flexible electronics because they allow current flow between semiconducting islands and other operating features. When ductile films on polymer substrates are strained in tension the substrate can suppress the catastrophic failure that allows for their use in flexible electronics and sensors. However, the charge carrying ductile films must be of an optimum thickness and microstructure for suppression of cracking to occur. In order to improve mechanical and electrical properties of these complex material systems, more work at characterizing the processing-structure-property relationships should be performed. Studies of strained films on polymer substrates tend to emphasize only the electrical properties and thickness effects more than the role of film microstructure or deformation behavior. The microstructure of the film not only determines the mechanical behavior but also influences the electrical behavior and could be optimized if studied in connection with the mechanical behavior. To address both the electro-mechanical and deformation behavior of metal films supported by polymer substrates, in-situ 4 point probe resistance measurements were performed with in-situ confocal scanning laser microscopy imaging of the film surface during cycling. The 4 point probe resistance measurements allow for the examination of the changes in resistance with strain, while the surface imaging permits the visualization of localized thinning and crack formation. Furthermore in-situ synchrotron tensile tests provide information about the stresses in the film and show the yield stress where the deformation initiates and the relaxation of the film during imaging. The combination of electrical measurements, surface imaging, and stress measurements allow for a complete picture of electro-mechanical behavior needed for the improvement and future success of flexible electronic devices.

9:00am **H2-1-4 Crystalline/Amorphous Metallic Multilayers – from Dislocations to Shear Bands***, **Marlene Mühlbacher,*** Montanuniversität Leoben, Austria*; C Gammer,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; F Spieckermann, C Mitterer, J Eckert,* Montanuniversität Leoben, Austria

Amorphous metallic coatings have recently emerged as promising thin film materials - thin film metallic glasses - due to their excellent chemical stability, good wear resistance and exceptionally high strength. Their mechanical behavior, however, is fundamentally different from their crystalline counterparts, due to the disordered structure lacking dislocations as carriers of plastic deformation. To investigate the different deformation and failure mechanisms, we have synthesized Zr- and Pd-based crystalline/amorphous multilayers with a total thickness below 1 µm and individual layer thicknesses below 100 nm by unbalanced dc magnetron co-sputtering from elemental targets. The microstructural variation is achieved by a change of deposition temperature or a change of composition (e.g. crystalline $Pd_{0.69}Si_{0.31}$ /amorphous $Pd_{0.80}Si_{0.20}$) established by different powers applied to the magnetrons. Nanomechanical samples are prepared in a focused ion beam instrument. Mechanical properties and their dependence on layer thickness and arrangement of the multilayers are investigated with a particular emphasis on *in-situ* tensile testing in the transmission electron microscope. This approach allows for a direct comparison of plastic deformation through the movement of dislocations and shear bands in the crystalline and glassy layers, respectively. Strategies for the prevention of sudden failure of the thin film metallic glass, e.g. by the confinement of shear bands between crystalline layers, are evaluated.

The tensile tests are complemented by *in-situ* and conventional nanoindentation and put into context with glass transition and crystallization temperatures of the thin film metallic glasses obtained by differential scanning calorimetry, thus presenting a comprehensive picture of the crystalline/amorphous multilayer system.

9:20am **H2-1-5 A Novel Method for the Preparation of Tensile Thin Film Specimens for In-situ Mechanical Testing in the TEM***, **Benoit Merle,** J Liebig, M Göken,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

A novel method was developed for the preparation of thin film micro-tensile specimens. Unlike most previous techniques, it does neither require the availability of a cleanroom nor that of expensive photolithographic equipment. It is based on a combination of focused ion beam (FIB) milling and electron-beam-assisted etching with xenon difluoride precursor gas. In contrast to existing FIB-based preparation approaches, the area of interest is never exposed to ion beam irradiation and a pristine microstructure is preserved. This is achieved by using a special shadow milling geometry with a thin silicon membrane simultaneously serving as a substrate and protective layer for the thin film of interest. A great advantage of the new method is that it enables the target preparation and mechanical testing of individual microstructural defects. The method was applied to nanotwinned Cu-Al as well as Au thin films. The fabricated tensile specimens were mounted on a push-to-pull conversion device and subsequently tested in-situ in the transmission electron microscope (TEM).

[1] Liebig, J. P., Göken, M., Richter, G., Mačković, M., Przybilla, T., Spiecker, E., Pierron, O.N., Merle, B.: A flexible method for the preparation of thin film samples for in situ TEM characterization combining shadow-FIB milling and electron-beam-assisted etching. Ultramicroscopy, 171:82-88 (2016).

9:40am **H2-1-6 Liquid Metal Embrittlement at the Micro-scale: Gallium FIB vs. Xenon FIB***, Y Xiao,* Laboratory for Nanometallurgy, ETH Zurich, Switzerland*; **Jeff Wheeler,*** Laboratory for Nanometallurgy, ETH Zürich, Switzerland

Micromechanical testing of structures fabricated using focused ion beam (FIB) has allowed significant progress to be made in understand the deformation and properties of small volumes of materials. However, the vast majority of FIB structures are machined using Gallium, which is known to embrittle many metals (e.g. Al, Cu and Fe) by weakening their grain boundaries. This has recently been shown to have a significant negative effect on the strength of micropillars of polycrystalline aluminum. Here we extend upon that work to investigate the effect of Ga FIB on the deformation and fracture properties of grain boundaries of several materials by comparing structures (micro-pillars and -cantilevers) made using both Xe FIB and Ga FIB.

10:00am **H2-1-7 Quantum Contact Mechanics for Tribology, Wear and Erosion*, Norbert Schwarzer,*** SIO, Germany

Erosional or tribological models and simulations do not only require a comprehensive mechanical contact model but also need to account for the principle uncertainties residing in the field.

It will been shown that the classical continuum mechanical and thus, also deterministic, concepts are not adequate if one intends to describe tribological processes like erosion, fretting, wear etc.

By incorporating quantum mechanical concepts via a principle scale dependent accessibility with respect to input parameters from measurement, surface roughness or even non-continuous composition, one does not only overcome such flaws in the classical approaches but also automatically incorporates a method to observe and actively control the influence of the uncertainty budget [1].

According to the classical quantum mechanics, the uncertainty is been accounted for by a “Planck” constant, only that this time, depending on the dimension of the problem, we end up with Planck-vectors or tensors instead of the classical scalar.

The way to go is cumbersome at the beginning, because it requires the principle quantization of the line element of a general continuous space, but the outcome is a very compact, rather general and powerful tool to handle practical applications.

As a byproduct, so it seems, also the quantization of the Einstein field equations can be achieved [2].

[1] N. Schwarzer: „Quantum Tribology – Part I: Theory“, www.amazon.com/dp/ B01CI4BI2E

[2] N. Schwarzer: „Recipe to Quantize the General Theory of Relativity“, www.amazon.com/dp/ B01LX664IF

10:20am **H2-1-8 Textile Nanocharacterization: Topography, Phase Imaging, and Nanomechanical Property Investigation of Polyester Yarn Interaction with Silicon Matrix***, B Kim, **Gerald Pascual**, K Lee,* Park Systems Corporation, USA

Textiles research and development is rapidly turning to nanomaterials to create new fabric blends that have increased performance for traits such as damage resistance, breathability, and even self-cleaning. To better inform materials design strategies, it is necessary to have a tool and techniques capable of measuring not only nanoscale topographies of material components, but their nanomechanical properties as well. Atomic Force Microscopy (AFM) is a solution well-suited to explore and characterize these traits. To this end, a silicon gel matrix and polyester yarn sample was prepared for examination with a commercial AFM system, the Park NX10 from Park Systems. Non-contact mode AFM from Park Systems was used to perform topography and phase imaging. Force-distance spectroscopy plus force-volume mapping was used for nanomechanical property characterization. The acquired data reveals that the hardness of the yarn is about 100 times greater than the matrix it is embedded in with forces being measured in nanonewton resolution and distances in micrometers. This investigation of the textiles sample is reflective of AFM’s effectiveness in allowing textiles researchers to explore the root, nanoscale causes of desirable macroscopic traits in novel fabric blends and further improve upon them.

10:40am **H2-1-9 A Nanoindentation System with Equivalent Capabilities in Both Normal to and Parallel to the Sample Surface***, **Warren Oliver**,* Nanomechanics, Inc., USA*; P Phani,* International Advanced Research Centre for Powder Metallurgy & New Materials, India*; K Johanns,* Nanomechanics, Inc., USA*; J Pethica,* CRANN, Trinity College Dublin, Ireland*; K Parks,* Nanomechanics, Inc., USA

An entirely new nanomechanical testing system has been built. The system retains the same measurement capabilities associated with high performance nanoindentation systems from which we have reported results in the past in the direction normal to the surface of the sample and adds the equivalent signals parallel to the surface. The same sensitivity, range and dynamic performance (including frequency specific experiments) are available simultaneously and continuously in both directions. The ability to measure not only load and displacement but stiffness and phase angle at specific frequencies parallel to the surface continuously and simultaneously with these same measurement in the normal direction has resulted in entirely new results concerning the onset of sliding between two bodies in contact. Unique new data concerning the initiation of slip at micro asperities, friction and wear, lubrication, scanning surface topology, mechanical property mapping and multidimensional characterization of structures can now be investigated. Specifics of the dynamic performance when each axis is actuated separately as well as simultaneously will be presented along with a number of examples of its use. A dynamic model that describes the system's behavior will also be presented.

11:00am **H2-1-10 The Effects of TIP Sharpness and Substrate Properties on Nanohardness Measurement in Thin Hard Coatings by FEM***, **Frantisek Lofaj**, D Nemeth,* Institute of Materials Research of SAS, Slovakia

FEM modelling of nanoindentation in the hard coating/softer substrate system revealed strong influence of the sharpness of the indenter tip on the hardness-indentation depth profiles resulting in the limited validity of the general 10% relative indentation depth rule. The result was attributed to the increase of the size of plastic field under the indenter with the increase of tip radius and the limits for the applicability of the nanoindentation tests with real (blunted) indenters were determined. Another important factor strongly affecting the hardness - depth profiles is the difference among the properties of the coating and substrate. These observations were confirmed experimentally on the corresponding depth profiles obtained in the continuous stiffness measurement mode on different W-C coatings deposited on steel and hardmetal substrates by HIPIMS and HITUS. The above limitations of nanoindentation in the determination of the nanohardness of thin films from the corresponding depth profiles are discussed.

11:20am **H2-1-11 Small Punch Testing for Mechanical Characterisation of a Free-standing CoNiCrAlY Coating***, **Hao Chen**,* University of Nottingham, China

In this study, the ductile-to-brittle transition temperature (DBTT) of a high velocity oxy-fuel (HVOF) thermally sprayed CoNiCrAlY (Co-31.7% Ni-20.8% Cr-8.1% Al-0.5% Y (wt%)) coating was investigated. To determine the DBTT, displacement controlled small punch tensile test (SPTT) and multi-step loading small punch test were employed between room temperature (RT) and 750 °C. At low temperatures, evidence of elastic-brittle behaviour was found but at high temperatures extensive yielding and plastic deformation occurred. The yield strength ranged from 1000-1500 MPa below 600 °C to less than 500 MPa above 650 °C and the elastic modulus was found to be approximately 200-230 GPa at 500 °C and 55 GPa above 700 °C, as evaluated via SPTT. The displacements obtained from multi-step loading SPT at each load increment were relatively small and similar at temperatures below 500 °C but a significant increase in displacement was noted at 600 °C. Test results gave a DBTT of this coating of approximately between 500-700 °C. Fractographic investigation showed that the fracture surface at RT exhibited flat, smooth features indicating brittle fracture whereas at 600 °C and above the main fracture mode was dominated by extensive ductile tearing.

Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 4-6 - Session H2-2

Advanced Mechanical Testing of Surfaces and Coatings

Moderators: Benoit Merle, Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Marco Sebastiani, University of Rome "Roma Tre"

1:30pm **H2-2-1 Mechanical Properties of High-strength Low-weight Truss Structures Fabricated by 3D Direct Laser Writing**, ***Ruth Schwaiger,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WBM), Germany **INVITED**

Cellular materials with designed architectures are fabricated with the goal to design new materials with high strength and low density. In our approach, polymeric truss structures with characteristic features in the micro-to-nanometer range are fabricated by 3D direct laser writing and then coated using thin film deposition techniques. Annealing treatments as well as deposition of alumina or metal coatings are shown to enhance the strength of the structures.

Nanomechanical testing methods are used to investigate the deformation behavior of the fabricated structures. As demonstrated by push-to-pull tensile tests, annealing can increase the material strength by up to a factor of 10. However, it is found that this increase of strength cannot be fully transferred to architected materials, such as tetrahedral truss structures, because of stress concentrations at the truss nodes. Failure of the truss structures due to buckling and subsequent fracture at the truss nodes as well as a pronounced recovery upon unloading was observed. Cyclic tests showed energy dissipation, which is a function of progressively failing ligaments. Deformation and failure as well as the strategies to improve the properties of 3D microarchitectures will be discussed.

2:10pm **H2-2-3 An improved Nanoindentation Method to Measure Residual Stress and Elastic Moduli of Freestanding Multilayer Thin Films*,* *Marco Sebastiani,*** *M Ghidelli,* Roma TRE University, Italy

In this work, we developed an improved nano-mechanical characterisation procedure of freestanding bilayer (Au-TiW) micro-cantilevers and double clamped beams, for applications as Radio Frequency (RF)-switches Micro-Electromechanical Systems (MEMS). The micro-beams are deflected by using nanoindentation in dynamic stiffness measurement mode, in order to extract the elastic modulus and the residual stresses of both layers. Firstly, the classic beam theory has been implemented for bilayer cantilevers enabling the extraction of elastic moduli. Then, residual stresses are estimated by deflecting double clamped beams, while implementing new analytical models for a bilayer system. The obtained elastic moduli are consistent with the average ones obtained for a single layer micro-cantilever and with nanoindentation results for TiW and Au homogeneous films. The residual stresses are in agreement with the values obtained from the double slot Focused Ion Beam (FIB) and Digital Image Correlation (DIC) procedure, providing an alternative and portable way for the assessment of residual stresses on composite double clamped micro-beams.

2:30pm **H2-2-4 *In Situ* FIB-SEM DIC and Synchrotron XRD Analysis of the Mechanical Degradation of a Uniaxially Loaded Copper-Tungsten Nano-Multilayer*,* *León Romano Brandt,*** *E Salvati, C Papadaki, H Zhang, S Ying, T Sui, A Korsunsky,* University of Oxford, UK

Thin coatings and multi-layers with individual layer thickness down to a few nanometres enable the design of materials with novel and carefully tailored thermal, mechanical, and functional properties. These properties arise as a consequence of the confinement of inhomogeneous mechanical, chemical and electromagnetic fields within nano-scale strata and nano-grains of material. External mechanical loading can cause structural damage and significantly decrease or undermine the performance of coating systems. It is therefore important to develop methods for quantifying material specific parameters, as well as attain a fundamental understanding of the mechanisms determining the mechanical response of thin films at the micro- and nanoscale and transform this fundamental understanding into generally applicable models.

The analysed copper-tungsten nano-multilayers with individual layer thicknesses of 18/6 nm and a total thickness of 240 nanometres are particularly attractive for applications as heatsinks in microelectronics. The micro- and nano-mechanical analysis of this material requires a variety of complex methods and techniques capable of precisely manipulating and resolving samples at these scales. *In situ* scanning electron microscopy (SEM) image sequences recorded during deformation of samples prepared by focussed ion beam (FIB) milling were interpreted using digital image correlation (DIC) to determine displacement and total strain fields. On this basis, a viable method is proposed for determining fracture toughness of thin nano-multilayers and other key properties of sub-micron thin films.

A very powerful tool for the determination of the elastic strain component of multilayers is synchrotron X-ray diffraction (XRD). We used this technique for *in situ* strain mapping regions of interest while applying stretching to the coating substrate. Based on the obtained strain maps, a description is proposed of the stress-strain state in hard brittle coatings on soft polymer substrates under substrate stretching.

2:50pm **H2-2-5 Synchrotron Nano-diffraction Studies of Ex-situ and In-situ Indented Thin Films: Microstructure and Stress Analysis*,* *Juraj Todt,*** Montanuniversität Leoben, Austria*; C Krywka,* Helmholtz-Zentrum Geesthacht, Germany*; M Burghammer,* European Synchrotron Ratiation Facility, France*; J Keckes,* Montanuniversität Leoben, Austria

Mechanical testing of small features such as thin films and surface regions is a challenging task, especially in the case of microstructurally complex systems exhibiting property gradients at the sub-micrometer scale. Since indentation is a popular technique, there has been considerable effort to model the rather complex underlying mechanical interactions. However, it has been difficult to find experimental validation for these numerical studies, due to the lack of adequate experimental methods.

In recent years cross-sectional scanning X-ray nano-diffraction at synchrotrons has been established as a powerful technique for structural analysis of thin films. Its key feature is a high spatial resolution, usually below 100 nm, offering insight into depth-gradients of phase composition, preferred orientation, morphology and stresses that evolve as a consequence of self-governed film growth or due to deliberate process control.

In the presented work, its capability to assess these sub-micrometer gradients is exploited as a means to study the microstructural changes and stresses induced during the indentation of thin films. This covers the extent, shape and magnitude of multi-axial stress fields during or after their formation, localized reorientation of grains, generation of defects, as well as their relation to the resulting failure modes. Multiple cases of multi-layered and monolithic metallic and ceramic thin films that were indented either ex-situ or in-situ will be discussed. Some of the presented cases will also be compared to respective FE analyses, highlighting areas for their improvement.

[1] Keckes J, Bartosik M, Daniel R, Mitterer C, Maier G, Ecker W, et al. (2012), X-ray nanodiffraction reveals strain and microstructure evolution in nanocrystalline thin films, *Scr Mater* **67**, 748–51.

[2] Stefenelli M, Daniel R, Ecker W, Kiener D, Todt J, Zeilinger A, et al. (2015) X-ray nanodiffraction reveals stress distribution across an indented multilayered CrN/Cr thin film *Acta Mater* **85**, 24-31.

[3] Zeilinger A, Todt J, Krywka C, Müller M, Ecker W, Sartory B, Meindlhumer M, et al. (2016) In-situ Observation of Cross- Sectional Microstructural Changes and Stress Distributions in Fracturing TiN Thin Film during Nanoindentation, *Sci Rep* **6**, 22670.

3:10pm **H2-2-6 Cross-sectional Microstructure and Mechanical Behaviour of As-deposited and Oxidised CVD TiB_2 Hard Coatings Determined by X-ray Nanodiffraction and Micro-mechanical Tests*,* *David Gruber,*** *M Tkadletz, N Schalk,* Montanuniversität Leoben, Austria*; B Sartory,* Materials Center Leoben Forschung GmbH (MCL), Austria*; C Mitterer, J Keckes,* Montanuniversität Leoben, Austria

In multilayered hard protective coatings used for industrial cutting operations, the functional behaviour depends on the properties of individual sublayers and interfaces.

In this contribution, mechanical properties, residual stresses and the cross-sectional microstructure of TiN/TiB_2 protective coatings on WC-Co substrates are analysed in as-deposited state and oxidised at 700°C in ambient air.

Synchrotron X-ray nanodiffraction is used to investigate gradients of phases and residual stresses as a function of coating depth in order to assess oxidation-induced changes in stress state and observe oxide formation.

In addition, in-situ micromechanical tests on micro-cantilevers, machined by focused ion beam milling of the TiB_2 and TiN sublayers are performed in the scanning electron microscope in order to determine Young's moduli and fracture stresses.

The experimental results indicate a complex nature of oxidation-induced degradation at the coating cross-section and allow to quantitatively evaluate changes in important coating parameters.

3:30pm **H2-2-7 Fundamental Mechanical Properties of Simple- and Pt/Ir-modified-Aluminide Diffusion Coatings after Thermocyclic Exposure***, **Ceyhun Oskay**, M Galetz,* DECHEMA-Forschungsinstitut, Germany*; H Murakami,* National Institute for Materials Science, Japan

The oxidation protection of Ni-based superalloys under service conditions relies on the mechanical and chemical stability of aluminide diffusion coatings, which provide the necessary Al-reservoir for the protective oxide scale formation. During exposure at high temperatures, the existing chemical gradient between the coating and substrate causes an alteration of the microstructure. Microstructural degradation of such coatings not only affects the chemical lifetime, but also influences the mechanical durability of the system. Therefore determination of the mechanical properties of simple- or modified-aluminide coatings is a significant step for precise lifetime assessment. The change in the microstructure is especially important for thin-walled components, for which the mechanical contribution of the coating gains importance.

In this study, simple aluminide coatings were deposited on four-point-bending flexural test samples of a 2nd generation Ni-based superalloy via a CVD-process. Pt- and Pt/Ir-modified aluminide coatings were manufactured on PWA 1483 samples via a two-step process involving electrodeposition and subsequent pack-aluminizing. Afterwards the samples were exposed to thermocyclic oxidation (1h cycles) at different maximum temperatures (highest 1100°C) for various durations (max. 1000 cycles). Fracture strain, hardness and elastic modulus were determined after the exposure at room temperature (RT) via four-point-bending flexural test with in-situ acoustic emission measurement and nanoindentation respectively. Consequently, the fundamental mechanical properties were correlated with the corresponding Al-concentration.

Al-depletion during thermocyclic exposure causes an increase in the fracture strain. Further depletion triggers the formation of the more ductile γ'-phase, through which the coating becomes able to deform plastically with the substrate at RT, rather than showing premature brittle fracture. Elastic modulus and hardness decrease within the single-phase region. However within the two-phase stability region, the formation of the γ'-phase causes an increase of both properties.

3:50pm **H2-2-8 Fast Nano-mechanical Property Mapping using XPM on Nano-crystalline Structures***, **Anqi Qiu**, D Vodnick,* Hysitron, Inc., USA

Surface properties of nano-crystalline materials have been studied intensively using various spectroscopy and microscopy techniques. But due to the sizes of the crystalline structures, it was difficult to map the deformation behaviors of nano-crystalline materials due to the continuum behavior of stress. With the development of ultra low noise XPM technique, nano-mechanical behaviors of nano-crystalline materials show good correlation between the mechanical behavior map and the crystallographic characterization. This gives a new direction of studying nano-crystalline plasticity and grain boundary mediated deformation.

Advanced Characterization Techniques for Coatings and Thin Films
Room Grand Exhibit Hall - Session HP

Symposium H Poster Session

HP-2 How Can the Icephobicity of an Engineered Surface be Screened by Means of Simple Laboratory Testing and Characterization?*, G de la Fuente, L Angurel,* CSIC-Universidad de Zaragoza, Spain*; C López-Santos, V Rico, A Borrás, A González-Elipe,* Instituto de Ciencia de Materiales de Sevilla (CSIC), Spain*; J Mora, P García,* ***Alina Agüero,*** Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Ice formation and accretion present serious safety issues for aircraft, the automotive industry, signalling devices, railway systems, buildings, wind energy conversion plants, terrestrial power lines and many others. Considerable effort has been devoted to tackle this crucial yet challenging issue, mainly by developing anti-icing coatings that, based on the idea that a non-wetting material would diminish the water-surface contact and avoid the ice formation, link the hydrophobic properties of the materials with a supposed anti-icing function. However, it has been demonstrated that this rule is not always true, as in very humid environments ice can form on superhydrophobic materials.

The Canadian-European project"Super-IcePhobic Surfaces to Prevent Ice Formation on Aircraft" (PHOBIC2ICE) aims at producing durable icephobic surfaces by means of surface engineering and/or coatings. One of the main challenges faced by this project is to achieve screening laboratory tests capable of establishing if a given coating or engineered surface shows promising anti-icing properties, before having to run complex and expensive icing wind tunnel (IWT) or flying tests. Most published work in this domain use the measurement of the wetting angle and on the superhydrophobicity level of the surfaces as a pass or not pass criterion for further testing, despite that hydrophobicity and icephobicity are not necessarily correlated. The present work evaluates a simple test developed within the project, for measuring ice accretion, and compares it with a series of other simple laboratory tests and characterization techniques such as wetting angle, contact angle hysteresis, freezing delay, and roughness. Various surface treatments have been investigated in an attempt to correlate the results of these test results and the icephobicity of said materials. On the second stage of PHOBIC2ICE, the results will be compared with those obtained in an icing wind tunnel and flight tests.

HP-3 Pushing the Envelope in Variable Temperature Nanoindentation: High and Cryogenic Temperature Measurements*, N Randall, M Conte,* Anton Paar TriTec, Switzerland*; J Schwiedrzik, J Michler,* EMPA, Switzerland*;* ***Pierre Morel,*** Anton Paar, USA

One of the primary motivations for development of instrumented indentation was to measure the mechanical properties of thin films. Characterization of thin film mechanical properties as a function of temperature is of immense industrial and scientific interest. The major bottlenecks in variable temperature measurements have been thermal drift, signal stability (noise) and oxidation of/condensation on the surfaces. Thermal drift is a measurement artifact that arises due to thermal expansion/contraction of indenter tip and loading column. This gets superimposed on the mechanical behavior data precluding accurate extraction of mechanical properties of the sample at elevated/cryogenic temperatures. Vacuum is essential to prevent sample/tip oxidation at elevated temperatures and condensation at cryogenic temperatures.

In this poster, the design and development of a novel nanoindentation system that can perform reliable load-displacement measurements over a wide temperature ranges (from -150 to 800 °C) will be presented emphasizing the procedures and techniques for carrying out accurate nanomechanical measurements. This system is based on the Ultra Nanoindentation Tester (UNHT) that utilizes an active surface referencing technique comprising of two independent axes, one for surface referencing and another for indentation. The differential depth measurement technology results in negligible compliance of the system and very low thermal drift rates at high temperatures. The sample, indenter and reference tip are heated/cooled separately and the surface temperatures matched to obtain drift rates as low as 1nm/min at 800 °C without correction. Instrumentation development, system characterization, experimental protocol, operational refinements and thermal drift characteristics over the temperature range will be presented, together with a range of results on different materials.

HP-4 Surface and Sub-Surface Damage in Si and Ge Crystals after Nano-Machining*,* ***Jozef Keckes,*** Montanuniversität Leoben, Austria*; Z Zaprazny, D Korytar, M Jergel, Y Halahovets, P Siffalovic,* Slovak Academy of Sciences, Slovakia*; C Ferrari, C Frigeri,* CNR-IMEM Institute Parma, Italy*; I Matko, J Drga,* Slovak Academy of Sciences, Slovakia*; P Vagovič,* DESY, Center for Free-Electron Laser Science, Germany

Nano-machining methods like single point diamond turning (SPDT) and fly cutting (FC) are used to fabricate high-quality active surfaces of X-ray crystal optics. In this contribution, experimental results from Ge and Si surfaces will be used to demonstrate sub-surface damage (SSD) of the crystal lattices after various machining steps. The machined surfaces are characterized using atom probe microscopy, transmission electron microscopy (TEM), focused ion beam milling, scanning electron microscopy and Raman spectroscopy. The results reveal that the SSD and residual stresses correlate with the machining conditions. The morphology of surface ripples as well as a periodic variation of Raman peak shift are observed and correlated. TEM results are used to demonstrate the influence of the machining on the cross-sectional lattice damage.

This work was supported by projects APVV-14-0745 and VEGA 2/0004/15 and FFG M-ERA.net project 841930 XOPTICS.

HP-6 Influence of Post-deposition Annealing on the Electrical Properties of Thin SiO2/a-Si:H/SiO2 Structures Obtained by Electron Cyclotron Resonance*,* ***David Mateos,*** Universidad Autónoma de Baja California, Mexico*; J Diniz,* University of Campinas, Brazil*; N Nedev, B Valdez, M Curiel,* Universidad Autónoma de Baja California, Mexico*; M Mederos,* Renato Archer Center for Information Technology, Brazil*; O Pérez, A Arias,* Universidad Autónoma de Baja California, Mexico

In this work results are presented for the deposition of thin multilayer structures, SiO2/a-Si:H/SiO2, by electron cyclotron resonance-chemical vapor deposition (ECR-CVD) technique. The ECR remote plasma systems present excellent characteristics that allow deposition of high quality uniform films at room temperature suitable for application in CMOS technology.

The depositions were carried out at an applied microwave power of 250 W under a gas pressure of 2.0 mTorr and a substrate temperature of 20°C. SiO2 film with thickness of ~6-8 nm were deposited using O2 and 2% SiH4 diluted in Ar as precursor gases. Hydrogenated amorphous silicon (a-Si:H) films with thickness of ~3-4 nm were deposited using the same flows of SiH_4 and Ar as in the case of SiO_2 but without O_2 flow. The films were deposited on p-type (100) c-Si substrates.

The film thicknesses in the multilayer structures were evaluated using the deposition rates of the a-Si:H and SiO_2. Individual layers of SiO_2 and a-Si:H were deposited on c-Si wafer and their thicknesses were determined ellipsometrically. As-deposited films were annealed at 800°C and 1100°C in N_2 atmosphere for 60 minutes.

Three-layer MOS structures were patterned by lithography and sintered in forming gas for 20 min. The influence of high temperature post-deposition annealing on the electrical properties of the structures was studied by current-voltage (I-V) and capacitance-voltage (C-V) measurements.

I-V measurements indicated that the high temperature annealing improves the gate dielectric properties. The C-V dependencies showed a correlation between the annealing temperature and the memory window of the structures. A possible explanation is that the high temperature annealing leads to structural modifications and formation of traps suitable to trap carriers. In addition, a strong improvement of the insulating properties of the SiO2 films was observed. Both changes may contribute to the observed memory effect. The obtained results show that the studied structures have a potential for application as gate insulators in non-volatile memory devices.

HP-7 Comparison of Three Methods for Ellipsometry Characterization of Thin Absorbing Films*,* ***Frank Urban,*** Florida International University, USA*; D Barton,* Retired, USA

Ellipsometry is a surface and film analytical technique which takes advantage of the fact that light reflecting from a surface undergoes a change in polarization state. The change in state results from the geometric structure and materials making up the reflecting surface. The predicted change in state can be determined through appropriate application of Maxwell's equations resulting in a mathematical model containing the surface descriptive parameters. In the common measurement scenario some of these parameters may be known and some, unknown, for example film thickness. Thus the method first requires fabrication of reflecting surfaces which result in tractable models. Next, measurements are made, at times spectroscopic, at multiple incidence angles, and on films of increasing thickness. Finally adjustments in the model and parameters are performed to put measurement and theory into agreement. It is well understood that these steps will depend upon the materials and thicknesses and other aspects of the reflecting surface. The purpose of the work to be presented is to make a direct comparison between different methods for determining the model and achieving agreement using the exact same films and measurements. The relative advantages and disadvantages of each method will be described. The three methods are that of Yamamoto which solves for pairs of measurements on growing films, the method in common use which seeks statistical agreement using the Levenberg-Marquardt algorithm to minimize mean square error, and the methods of the authors in the n-k plane which cast the problem into a deterministic mathematical expression which is solved numerically, typically by Newton-Raphson. Three different materials systems are explored; NiOx/Si, Cr/Si, and Ni/BK7. In each case the film is absorbing and ranges from a few nanometers up to approximately 30 nm in thickness. Differences in resolution, accuracy, model specificity, and difficulty of application will be presented.

Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 4-6 - Session H1

Advanced Microstructural Characterization of Thin Films and Engineered Surfaces

Moderators: Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

8:00am **H1-1 Imaging Cross-sectional Structure-property Relationship in Thin Films***, **Jozef Keckes**,* Montanuniversität Leoben, Austria **INVITED**

Peculiarity of physical properties of nanocrystalline thin films resides in (i) the small crystalline size typically below 100 nm resulting in a variety of size effects, (ii) a high volume fraction of grain boundaries and (iii) a presence of gradients of microstructure and residual stresses. Those gradients may originate (i) from self-organized film growth far from the thermodynamic equilibrium, (ii) from the intentionally varying deposition conditions and/or (iii) from the inhomogeneous thermal and/or mechanical loads induced during the film service. In order to understand and optimize the functional behavior of the thin films, it is necessary (i) to analyze the properties of thin film distinct regions, like nucleation layers, interfaces and grain boundaries, and (ii) to reveal cross-sectional structure-property relationships.

In this contribution, experimental results from gradient hard and metallic thin films (e.g. TiAlN, CrN, Diamond, W, TiN/SiO_x) are discussed. The films are analyzed using a variety of novel analytical techniques developed by the group in last 5 years. Primarily, cross-sectional X-ray nanodiffraction using monochromatic point and pencil X-ray beams with a diameter or a thickness down to 30 nm was used (at ID13 of ESRF and at P03 of PETRA III) to resolve depth-resolved evolution of phases, texture, crystallite sizes and the first-order stresses across thin film cross-sections. The observed gradients are correlated with the varying film deposition conditions, providing an opportunity to optimize deposition processes. Additionally, results from strain and microstructure characterization (i) in in-situ indented TiN and (ii) in multilayered CrN-Cr thin films after wedge indentation are presented to demonstrate the correlation between the present (i) microstructure, (ii) recorded load-displacement curves as well as (iii) stress concentrations. Additionally, for a graded nanocrystalline TiAlN thin film, the comprehensive characterization of cross-sectional structure-property relationships will be used to analyze the correlation between sub-micron depth variations of fracture stresses, hardness and elastic moduli on one side, and phases, crystallite sizes, crystallographic texture, Ti/Al ratio and residual strain on the other side. Finally, the cross-sectional approach will be used to indicate the possibility of functional optimization of thin films through cross-sectional design.

8:40am **H1-3 Synchrotron and Transmission Kikuchi Diffraction Characterization of Deformed Multilayer Thin Films on Polyimide***, **Mikhail Polyakov**, X Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; P Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nano metallic multilayers (NMMs) are materials which consist of multiple nanometer-thick layers of different metals. NMMs are present in a variety of applications, from protective coatings to electronics to x-ray mirrors. However, the deformation mechanics of such materials, which are especially relevant for protective coatings and electronics on flexible substrates, are difficult to determine for several reasons. Firstly, the small grain sizes and layer thicknesses (<50 nm) limit the use of techniques with larger resolution limits, most notably Electron Backscatter Diffraction (EBSD). In addition, the small layer thicknesses translate to small scattering volumes for X-ray diffraction techniques, which can result in prohibitively long data collection times.

To address these specific limitations, additional characterization techniques were used. The first is Transmission Kikuchi Diffraction (TKD, also referred to as transmission-EBSD or t-EBSD). The technique is similar to EBSD in that one can map grain orientations over a large area, but it utilizes the transmitted diffraction patterns rather than the backscattered diffraction patterns. This results in an improved spatial resolution of less than 10 nm, allowing for the characterization of layers and grains with characteristic lengths below 50 nm, before and after deformation.

The second technique used was in-situ synchrotron XRD of tensile tested films. The brilliance of the synchrotron X-ray source allows for much shorter recording times than for a standard X-ray source. Therefore, a series of diffraction patterns can be collected in a reasonable amount of time during the tensile testing of thin multilayered films. Since the diffraction rings for the different materials can be distinguished, the stress for the different materials can be determined individually. In this way, the deformation of the layers can be decoupled and the contributions of the individual materials to the overall deformation behavior can be calculated.

We have demonstrated the differing load sharing contributions from varying layer thicknesses for Cu/Nb nano multilayers on polyimide [1], and the results will be compared with the deformation of Cu/Zr and Cu/CuZr multilayer samples. With Cu/Nb, Cu/Zr, and Cu/CuZr multilayers, a variety of crystal structures are present, resulting in differing deformation mechanisms.

[1] Polyakov, Mikhail N., Jochen Lohmiller, Patric A. Gruber, and Andrea M. Hodge. Advanced Engineering Materials Adv. Eng. Mater. 17.6 (2014): 810-14

9:00am **H1-4 Advanced EBSD and *in-situ* EBSD Techniques for Microstructure, Crack, Fatigue, and Plastic Deformation Characterization in Metals and Thin Films***, J Ast, Y Guo, M Polyakov, J Schwiedrzik, G Mohanty, J Michler, **Xavier Maeder**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The measurement of characteristics such as crystal structure, crystallographic orientation, grain dimension, and residual stress is fundamental for evaluating thin films and coatings and correlating their structures with their mechanical, chemical, or thermal properties. For such analyses in small volume materials, X-ray diffraction techniques and transmission electron microscopy are generally considered to be the tools of choice. Electron backscatter diffraction (EBSD), which can be combined with cross correlation techniques (HR-EBSD), offers the advantage of providing crystal orientation maps from which phase, grain size, grain shape, grain boundary type, texture, residual stress, and crystal defects can be determined with a resolution of 50nm. In addition, Keller and Geiss have recently demonstrated that EBSD patterns can be acquired from a thin film specimen using transmitted electrons in the SEM [1] (Transmission Kikuchi-Diffraction [TKD] or transmission-EBSD), thus improving the lateral resolution of the technique by an order of magnitude, reaching sub-10nm resolution, making it suitable for nano-crystalline materials. We applied transmission-EBSD to characterize the microstructure of PVD and electrodeposited materials. Crystallization and twinning processes have been studied for several materials, such as nanocrystalline Ni, CuNi, CuAl, and pure Cu, and the observed structures have been linked to their mechanical proprieties. We have also applied EBSD and HR-EBSD techniques together with *in-situ* micro-mechanical testing to better assess the deformation mechanisms in metals and coatings. The detailed microstructure, plastic zone size, dislocation mobility, strain, and stress can be mapped at successive deformation steps in the materials. Examples will be given for micro-cantilever bending and micro-pillar compression.

References:

[1] R.R. Keller, R.H. Geiss, *Journal of Microscopy* 2012, 245, 245–251.

9:20am **H1-5 Characterization of the Porosity of Silicon Nitride Thin Layers***, **Thomas Barrès**, H Montigaud,* Saint-Gobain Recherche, France*; O Stephan,* Université Paris-Sud, France*; B Tribollet,* Université Pierre et Marie Curie, France*; Y Cohin,* Saint-Gobain Recherche, France*; M Boinet,* Saint-Gobain, USA

Silicon nitride (SiN_x) is commonly used as a dielectric thin film (10 to 100 nm) within stacks deposited by magnetron sputtering in the glass industry. The porosity of such thin films can be detrimental to the product durability and performances upon ageing [1].

The nanostructural characterization of silicon nitride thin films has been previously carried out by Transmission Electronic Microscopy (TEM) [2]. Thanks to several microscopy techniques such as TEM, Scanning Transmission Electronic Microscopy in High Angle Annular Dark Field mode (STEM HAADF), and Electron Energy Loss Spectroscopy (EELS), we are able to give a quantitative description of the porosity in SiN_x layers at the nanometre scale. In addition to purely topographic characteristics, EELS and HAADF measurements give access to the local composition and atomic density in the thin film. The 3D morphology of the pores was determined by observing the sample from different incidences (plane-view and cross sections obtained by means of FIB lamella).

In parallel to the microscopic approach, we estimated the porosity at a larger scale as well as the through-porosity total fraction, by using Electrochemical Impedance Spectroscopy (EIS) measurements. Impedance measurements have a high sensitivity to the pore distribution in the layer [3], providing a complementary point of view on the layer morphological characteristics to the one offered by TEM.

Finally, the evolution of the layer nanostructure is studied as a function of the SiN_x deposition parameters allowed by reactive magnetron sputtering (deposition pressure, sputtering rate, and plasma composition) as well as final characteristics (density, thickness or intrinsic stress).

References :

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9:40am **H1-6 Microsecond-Scale Chemical Reactions at Interfaces in Thermal Spray Coatings***, **Anh Tran**, M Hyland,* The University of Auckland, New Zealand

The possibility of extremely rapid chemical reactions at interfaces between molten metal droplets and metal substrates in thermal spray coatings is reported in this study. Nickel single molten droplet was deposited on different substrates including stainless steel, chromium and titanium at either room temperature or 300 °C by plasma spray. The splat morphology and splat-substrate interfaces were characterised using FIB and TEM. Substrate's element was found to diffuse into the nickel splat, but not vice versa. Thin layers of mixed oxides were detected at the interface of nickel droplet deposited on either chromium or stainless steel substrate, but not on titanium substrate. Instead, a relatively thick intermetallic layer with the thickness up to 1 µm composing of three different phases of $TiNi_3$, TiNi, and Ti_2Ni was found along the entire Ni-Ti interface. We also found that the chemical reactions to form interfacial layers occurred after the splat solidified, thus it is not involved in the way droplet spread on the solid surface and subsequent splat-substrate bonding.

10:00am **H1-7 Thermal Stability of Expanded Austenite formed on a DC Plasma Nitrided 316L Austenitic Stainless Steel***, **André Tschiptschin**, A Nishikawa, L Varela,* University of São Paulo, Brazil*; C Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil

Expanded austenite formed during low temperature plasma nitriding of austenitic stainless steels is known for its excellent wear and corrosion resistance especially when working in systems where galling, erosion-corrosion, cavitation-erosion and pitting corrosion resistance are a major concern. These wear and corrosion properties may degrade by exposure of the surface hardened steel to high temperatures, between 400 °C and 700 °C. In the present work, DC low temperature plasma nitrided 316L austenitic stainless steel (400 °C for 20 hours) was heated up to investigate the stability of the expanded austenite layer in the range 400 °C < T < 700 °C. Time-resolved X-ray diffraction experiments were undertaken in a thermomechanical simulator coupled to the Brazilian National Synchrotron Light Source. Two series of experiments were carried out: a) isothermal treatments conducted at temperatures between 400 and 600 °C for 4h and b) a continuous heating experiments from room temperature up to 700 °C, with a heating rate varying from of 6 °C/min to 60 °C/min. Results show that during the isothermal heat treatments, expanded austenite remains approximately stable up to 400 °C, without losing nitrogen and maintaining its lattice parameter. For isothermal holding temperatures higher than 450 °C a continuous decrease in expanded austenite in the time span of the experiments is observed, presumably due to diffusion of nitrogen to the matrix. This phenomenon is followed by formation of ferrite and chromium nitrides precipitation. In the continuous heating experiments expanded austenite decomposition into three products is observed: ferrite, austenite, and nitrides. As expected from thermal an activated reaction, the critical temperature of this transformation is dependent on the heating rate. At the heating rate of 12 °C/s the initial 0.385 nm expanded austenite lattice parameter increased up to 0.3875 nm at 425 °C due to thermal expansion, indicating an average thermal expansion, over the analyzed expanded austenite layer, of 5×10^{-5} K^{-1}. This value is much lesser than the values reported for the thermal expansion coefficients of the fcc austenitic phase in austenitic stainless steel $K = 15 \times 10^{-5}$ K^{-1}, indicating that expanded austenite is also losing compressive residual stresses during heating.

Author Index

Bold page numbers indicate presenter