Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 1-3 - Session H1

Spatially-resolved Characterization of Thin Films and Engineered Surfaces

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

9:00am **H1-4 Spatially Resolved Depth Profiling Of Residual Stress By Micro-Ring-Core Method*, Marco Sebastiani,*** Roma TRE University, Italy

In this presentation, we will show some fundamental advances to the depth profiling capabilities for micro-scale ring-core focused ion beam (FIB) method. A new model, based on a single variable eigenstrain influence function approach, is developed and validated by comparison of FIB-DIC experimental results with synchrotron nano-diffraction experiments on the same reference sample (TiN PVD coating deposited by MS-PVD).

To this end, we revisit and revise the classical integral method proposed over quarter of a century ago. Instead of focusing on the residual stress that varies with every increment of hole-drilling, we concentrate on the reconstruction of eigenstrain, the invariant source of residual stress, and establish that the eigenstrain depth profile can be reconstructed by compact direct calculation, obviating the need for matrix formulation of the integral equation.

The method's sensitivity and robustness is further improved by the rational combination of multiple datasets obtained using different ring-core diameters. In this way, the approach has been shown to achieve depth resolution better than 50nm, opening up the prospect of reliable residual stress analysis at the nanometer scale.

9:20am **H1-5 Quantitative Depth Profiling from the First Nanometers Down to the Substrate within Minutes using RF GD-OES*, Philippe Hunault,*** HORIBA Instruments, USA*; M Chausseau, K Savadkouei,* HORIBA Scientific, USA*; P Chapon, S Gaiaschi,* HORIBA Scientific, France

Glow Discharge Optical Emission Spectrometry (GD-OES) provides direct measurement of the chemical composition of materials as a function of depth and can be used to characterize various coatings, made of both thin and thick layers, conductive or non-conductive materials.

It consists in a pulsed radiofrequency glow discharge plasma source that is sputtering a large area of the material of interest and real time detection by a high resolution optical spectrometer of the sputtered species excited by the same plasma. All elements from H to U can be measured using this technique.

With its capability to perform depth profiling 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.

Recent developments made possible using GD-OES for the direct determination of layer thickness and also for the analysis of odd shape samples.

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. How this technique can be used for Quality Control for the Aluminum packaging industry will also be shown with the help of real examples. Finally, we will discuss the latest results obtained for the characterization of the various coatings applied on drill bits which is a challenging sample by its shape and size.

9:40am **H1-6 Analysis of Thin Film Surface Stress Distribution using Raman Spectroscopy near Cohesive Cracks During Bending Tests*, Newton Fukumasu,*** *G Francisco, R Souza,* University of São Paulo, Brazil

Stress distribution in a thin film is an important tool to control system performance in many applications. Usually, compressive stresses improve the wear behavior of the system, but the higher the compressive stresses, the higher the probability of coating adhesive failure. Stress calculation is based on the measurement of strain and present several pitfalls, frequently related to the elastic constants selected to correlate stains and stresses. This work aims contributing with the analysis of these constants in micro-Raman spectroscopy analyses. To this end, this work presents a technique to study the spatial distribution of the stresses at a coating surface near cracks generated by tensile stresses during bending tests. Literature reports that the stress state varies as a function of the distance from coating cohesive cracks, indicating that stresses are zero near the cracks. Local strains were measured based on the shift of the Raman spectrum. Measurements were conducted for a coated system composed of metal nitride films, deposited by sputtering, and ductile substrates. The stress evolution during the bending tests was reproduced numerically by means of simulations using the finite element method (FEM). Results were analyzed based on the correlation of the shift of the Raman spectrum and the stress evolution in bending tests, both during and after the test.

10:00am **H1-7 *In situ* Nanomechanical Characterization of Transition Metal Carbides***, M Chen,* ETH Zurich, Laboratory for Nanometallurgy, Switzerland*; D Sangiovanni,* Linköping University, IFM, Germany, Sweden*; J Wheeler,* ETH Zurich, Laboratory for Nanometallurgy, Switzerland*; **Suneel Kodambaka**, G Po,* University of California Los Angeles, USA **INVITED**

Refractory transition-metal carbides, owing to a mixture of ionic, covalent, and metallic bonding, exhibit high hardness, high stiffness, good resistance to wear, ablation, and corrosion, high-temperature mechanical strength along with good electrical conductivity. While these materials are exceptionally hard, their room-temperature structural applications have been limited by their brittleness. However, existing literature suggests that these carbides are not intrinsically brittle. Our recent nanomechanical tests carried out on sub-micrometer size carbide crystals have shown that these transition-metal carbides can undergo plastic deformation at room temperature.

In this talk, I will present results from our studies focused on understanding the mechanical deformation mechanisms operating in NaCl-structured TaC single-crystals. Using a combination of *in situ* scanning-electron-microscopy-based uniaxial micro-compression tests, *ab initio* molecular dynamics simulations conducted at temperatures up to 873 K, along with finite-element based modeling of discrete dislocation and crack dynamics, we determine the mechanisms leading to slip, dislocation nucleation and motion, and crack formation in TaC single-crystals. Our results provide new insights into the role of crystal orientation, size, and temperature on the correlation between plasticity and fracture in this class of materials.

Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 1-3 - Session H2

Advanced Mechanical Testing of Surfaces, Thin Films and Coatings

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

1:30pm **H2-1 In Situ Observation of Strain Transfer and Crack Formation in Evaporated and Printed Thin Films and Devices on Compliant Substrates***, **Patric Gruber,*** Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-WBM), Germany

Compliant substrates enable the fabrication of flexible electronics for numerous applications like flexible displays, solar cells, batteries or wearable/biocompatible electronics. However, the reliability of such devices is limited by the stretchability of the inorganic components. So far, little experimental work has been carried out to investigate the mechanical properties of thin inorganic films on compliant substrates at high strains and cyclic loading. Here, we present experimental results for the flow stress, fracture strain and fatigue behavior of evaporated and printed Ag films as well as printed thin film transistors on compliant substrates. The film systems have been tested by a synchrotron-based tensile testing technique (up to 10% total strain) as well as cycling loading (50 Hz, strain amplitude up to 2.5%) and have been characterized by SEM and FIB microscopy. The synchrotron experiments yield the stress evolution and strain transfer within the film systems whereas the cyclic tests give the fatigue lifetime. On the other hand, *in situ* electro-mechanical testing, *in situ* tensile tests in the SEM and stationary FIB investigations reveal the evolution of electrical performance, crack morphology and crack density as well as fatigue damage in the individual films. First, results of electro-mechanical testing of printed and evaporated Ag films will be presented. Electrical conductivity and mechanical reliability are investigated with respect to the inherently nanoporous microstructure, and are compared to those of evaporated Ag films of the same thickness. It is shown that there is an optimized nanoporous microstructure for inkjet-printed Ag films, which provides a high conductivity and improved reliability. It is argued that the nanoporous microstructure ensures connectivity within the particle network and at the same time reduces plastic deformation and the formation of fatigue damage. Furthermore, results on printed In_2O_3 thin film transistors are presented. Here, the interplay of the polymer substrate and solid polymer electrolyte with the metallic and ceramic interlayers within the transistor structure will be discussed based on the strain evolution within the individual layers determined from the *in situ* synchrotron experiments.

1:50pm **H2-2 Comparison of Different Methods for the Investigation of Thin Film Adhesion***, **Felix Schiebel,*** Fraunhofer Institute for Mechanics of Materials IWM, Germany*; C Eberl,* University of Freiburg, Germany

The reliability of power electronic devices (e.g. in solar industries and electric automotive applications) depends strongly on their electrical and mechanical interconnections. Thin metallic films deposited on semiconductor substrates are used to improve the connection at its most critical interface. The performance of these thin films, with dimensions typically of a few hundred nanometers, therefore greatly influences the reliability of the entire device.

To evaluate the adhesion of such films, a typical stack of thin metallic films consisting of an adhesion layer, a solderable NiV layer, and an Au oxidation protection layer was deposited on an Si semiconductor substrate. Several experimental methods (e.g. cross sectional nanoindentation (CSN) and scratch test) have been implemented to evaluate the adhesion in both the as-deposited state and an annealed state. The results of those measurements will be used to discuss the influence of the annealing on the adhesion and also on the measurement technique.

Furthermore, a new experimental setup will be presented which allows monitoring the delamination during CSN experiments with two separate cameras. The captured image series provide new experimental data which can be used to further improve fracture toughness calculations and to gain a deeper insight in delamination processes, allowing more the design of more reliable devices in the future.

2:10pm **H2-3 Electro-Mechanical Characterization of Functional Thin Film Metallic Glasses***, M Mühlbacher,* Montanuniversität Leoben, Austria*; O Glushko, **Christoph Gammer,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; C Mitterer, J Eckert,* Montanuniversität Leoben, Austria

Thin film metallic glasses, which have a signature disordered structure with metallic bonding characteristics, are starting to emerge as functional materials. To investigate their electro-mechanical behavior, we prepare binary metallic PdSi thin films with varying thicknesses on the order of 5-300 nm by co-sputtering from elemental Pd and Si targets in an unbalanced DC magnetron sputtering device. In order to achieve amorphous film growth on Si(001) and flexible polyimide substrates, deposition proceeds without external substrate heating and film composition is chosen close to the deep eutectic composition in the Pd-Si phase diagram.

Selected samples deposited on flexible substrates are analyzed in a tensile testing set-up with *in-situ* resistance measurements. The strain at which cracks start to form in the brittle amorphous films can be determined exactly as the point where resistance starts to increase. Simultaneous confocal laser scanning microscopy of the strained samples provides more information on the failure mode. In thicker PdSi thin film samples, characteristic shear bands are evident with a 45° angle to the straining direction in addition to large cracks normal to, and film delamination in the form of buckles parallel to the tensile direction after straining to 10%. With decreasing PdSi film thickness down to 5 nm, a more ductile fracture behavior is observed. This is explained by a plasticity size effect, where deformation changes from a highly localized to a homogeneous mode due to geometric limitations. These findings are complemented by *in-situ* tensile tests of free-standing PdSi films in a transmission electron microscope. The gained understanding of the interplay of electro-mechanical properties in functional thin film metallic glasses will contribute to a successful application of these materials in future microelectronic devices.

2:30pm **H2-4 New Pull-off Tensile Tests for Adherence Assessment in Concrete-formwork Coated and Uncoated Contacts***, **Nicolas Spitz,*** Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; N Coniglio, M El Mansori,* Arts et Métiers ParisTech d'Aix-en-Provence, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; A Montagne,* Arts et Métiers ParisTech de Lille, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France*; S Mezghani,* Arts et Métiers ParisTech de Châlons-en-Champagne, Laboratory of Mechanics, Surface and Materials Processing (MSMP-EA7350), France

Nowadays buildings construction is performed by pouring concrete into molds called formworks that are usually prefabricated metallic modules. Defects such as stripping may possibly form during the removal of the formwork if the interfacial bonding between the concrete and the formwork is high. Making use of a new pull-off tensile test designed in our laboratory, a correlation has been established between the formwork superficial functional signatures and its adherence susceptibility to concrete. The originality of this near-to-surface test was to characterize the concrete-to-formwork adherence by measuring the required force to pull the concrete from the formwork surface. The design of the test coupon was validated by finite element analysis that proves the small deformation of the tested formwork specimen under the tensile loading and the homogeneity of the applied tensile stress at the interface. The interfacial bonding to concrete has been compared between bare and coated formwork. Both metallic and polymer coatings have been studied. The analyses of the pull-off test results enabled us to understand the bonding mechanisms at the concrete-coating interfaces. The pull-off tensile test was proven capable of ranking formwork coatings according to their adherence to concrete.

2:50pm **H2-5 In-situ-squared: Combined Electro-mechanical Behavior of Thin Films with One Experiment***, **Megan Cordill,*** Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria **INVITED**

Studying the combined electro-mechanical properties of thin metal films on polymer substrates under mechanical load is one way to advance flexible electronic technologies. Ductile films and lines allow current flow between semiconducting islands and other operating features, thus are an integral part of flexible electronics. Flexible electronics also contain brittle layers which can improve adhesion, protect again corrosion or have semiconducting properties. When films on polymer substrates are strained in tension the substrate can suppress some of the catastrophic failure that allows for their use in flexible electronics and sensors. However, the interplay between the different layers can be very different compared to similar films on rigid substrates. In order to improve mechanical and electrical properties of these complex material systems, more work at characterizing the processing-structure-property relationships as well as the thin film architectures should be performed. Studies of strained films on polymer substrates tend to emphasize only the electrical properties or fracture strains effects more than the role of film thickness or multilayer behavior. The thickness of a ductile film will influence the mechanical behavior but also the electrical behavior, while even brittle thin metal layers can greatly affect the failure of ductile films. To address 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 films surface during uni-axial tensile straining. The 4 point probe resistance measurements allow for the examination of the changes in resistance with strain of the more deformable layer, 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 individual films 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 complex flexible electronic devices.

3:30pm **H2-7 Mechanical Behavior of Ductile/Brittle Multilayers Studied with In-situ Straining Methods***, **Patrice Kreiml**, M Rausch, V Terziyska,* Montanuniversität Leoben, Austria*; H Köstenbauer, J Winkler,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria*; M Cordill,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria

Mo thin films, which are frequently used as back-plane electrodes and as source/drain in thin film transistors, are inherently brittle compared to the electrical charge carrying ductile Cu or Al films. To improve the fracture behavior of stacks containing Mo layers for future flexible devices, and thus the reliability of the whole device, an optimum ductile/brittle layer thickness ratio is necessary. In this work the electro-mechanical behavior of multilayered Al/Mo thin films grown by dc magnetron sputter deposition on polyimide substrates is investigated. Various combinations of thicknesses for bi-layer and tri-layer architectures were evaluated (films of 50 to 450 nm thickness with different ductile/brittle layer thickness ratios). For a comparison of the behavior of the thin films, a combination of in-situ mechanical testing with electrical measurements, X-ray diffraction and 4-point probe resistance techniques were employed. In order to correlate the mechanical and electrical properties and to better understand the connection between crack onset, crack evolution and electrical resistance of the Al/Mo multilayers, in-situ confocal laser scanning microscope imaging was also performed. From X-ray diffraction data, individual film stresses during straining were determined, demonstrating that the ductile film thickness will dictate when through thickness cracks form in the multilayer. Once through thickness cracks form, the electrical conductivity deteriorates quickly and the multilayer stack can be considered failed. The combined in-situ testing also illustrates how brittle layers can cause typically ductile films to behave in a brittle manner due to the fact that cracks initially form in the brittle layers that act as stress concentrators in the ductile films. It will be shown that an optimized film architecture will improve the electro-mechanical behavior for flexible electronic applications.

3:50pm **H2-8 Fracture Behavior of Nanocrystalline BCC High-Entropy Alloys***, Y Xiao, H Ma, R Spolenak, **JeffreyM. Wheeler**,* ETH Zurich, Laboratory for Nanometallurgy, Switzerland

Refractory high-entropy alloys (HEAs) have attracted significant attention due to their superior mechanical properties at elevated temperature [1]. However, most of them are brittle and suffer from low ductility and toughness at room temperature, and their usage is limited due to the inadequate fracture-resistance property. Grain boundaries play an important role in the extraordinarily high temperature strength and stability [2] of bcc HEAs and can also be potential sites for fracture. Here, strongly textured, columnar and nanometer-size grains NbMoTaW HEA thin films with and without ion beam assisted deposition technique are produced. Mechanical properties, especially fracture toughness are determined by in situ micro-pillar and micro-cantilever tests. Further characterization is conducted by high-resolution SEM images and TEM analysis.

References

[1] O.N. Senkov, et al., Intermetallics, 19 (2011) 698-706.

[2] Y. Zou, et al., Nano Lett, 17 (2017) 1569-1574.

4:10pm **H2-9 Recent Advanves in Microcantilever Bending Experiments***, **Karsten Durst**,* Physical Metallurgy, TU Darmstadt, Germany*; M Göken,* University Erlangen-Nürnberg, Germany*; J Ast,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland **INVITED**

Microcantilever bending experiments are becoming more prominent in testing the local fracture toughness in a wide variety of materials. By focused ion beam milling or other techniques, a notched cantilever with micron sized dimensions is milled into a region of interest of a bulk material or thin coating. By loading the cantilever with a nanoindenter, a crack is nucleated at the notch tip and propagated through the sample and the fracture toughness can be evaluated at the local length scale. Applying conventional fracture mechanics approaches, the local critical stress intensity of the material is determined. With the presentation recent advances in the technique will be presented, focusing on elastic plastic fracture mechanics and crack tip plasticity.

4:50pm **H2-11 Temperature and Loading Rate Influence in Micro-Scale Fracture Experiments***, J Ast,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Schwiedrzik,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wehrs,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Michler,* EMPA, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; **Xavier Maeder**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The process zone or plastic zone around a loaded crack tip can significantly influence the fracture behavior of a material. Especially in micro-scale specimens, the plastic zone size may make out a large share of the sample volume and lead to a different fracture behavior than the one usually observed for macroscopic samples of the same material. Furthermore, the theoretical description of the plastic zone according to Irwin is not valid for single crystals. Therefore, a characteristic elastic-plastic fracture behavior is observed depending on crystallographic sample orientation and slip system activation. It is the aim of the study to give insight into the fracture process and behavior in micro-scale specimens in the presence of crack tip plasticity.

Notched micro-cantilevers were prepared by focused ion beam (FIB) milling in a tungsten single crystal. This material has nearly perfect elastic isotropy, a limited amount of activated slip systems and detailed knowledge of the macroscopic fracture behavior is available [1]. The cantilevers have dimensions of 25 µm in length, 5-7 µm in thickness and crack length to thickness ratios a/w of ca. 0.4. Loading rate and temperature are known to influence the fracture behavior decisively in bcc metals. Therefore displacement-controlled fracture tests were performed inside a scanning electron microscope in the temperature range between -100°C and 500°C. Applying the recently presented J-Integral technique [2] to plot continuous crack resistance curves, the fracture toughness and brittle-to-ductile transition (BDT) temperatures, which depend on the applied loading rate, were determined. This allows a thorough investigation of the activation energy of the BDT at the micro-scale.

Crack tip plasticity before and during crack growth was investigated by high-resolution electron backscatter diffraction measurements (HR-EBSD) on FIB cross-sections of the micro-cantilevers after mechanical testing. Plastic zones, which are strongly depending on the activated slip systems, and plastic strain gradients in terms of geometrically necessary dislocations were quantified and linked with the observed BDT behavior. Transmission electron microscopy was used to confirm the EBSD results and to provide dislocation analysis.

[1] P. Gumbsch, J. Riedle, A. Hartmaier, H.F. Fischmeister, Controlling Factors for the Brittle-to-Ductile Transition in Tungsten Single Crystals, Science. 282 (1998) 1293–1295.

[2] J. Ast, B. Merle, K. Durst, M. Göken, Fracture toughness evaluation of NiAl single crystals by microcantilevers - a new continuous J-integral method, Journal of Materials Research. 31 (2016) 3786–3794.

5:10pm **H2-12 Investigating the Local Fatigue Properties of Materials in Small Dimensions by Dynamic Micropillar Compression***, **Benoit Merle**,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany

A novel method was develop in order to investigate the local fatigue properties of ultrafine-grained copper on the micrometer-scale up to the high cycle fatigue (HCF) range, relying only on widely available nanoindentation hardware. This breakthrough was achieved by combining the widely used micropillar compression method with the fast actuation

(40 Hz) provided by the continuous stiffness measurement (CSM) module, originally intended for pyramidal nanoindentation. Cyclic testing was performed at constant nominal stress amplitude for up to several million (3.10^6) cycles. The resulting strain amplitude was directly recorded and the plastic strain was evaluated from the phase angle measured by the lock-in amplifier during testing. Defining a threshold for strain amplitude decrease as failure criterion further enabled the determination of S-N curves. The fatigue behavior of the tested ECAP copper micropillars was found to be dominated by cyclic softening, which is in line with previous macroscopic observations on similar samples. The calculated plastic strain amplitude also matches the literature data closely. Generally, the new method has a great potential for studying the local cyclic effects taking place at interfaces in complex micro-architectured materials and coatings.

Advanced Characterization Techniques for Coatings and Thin Films
Room Grand Hall - Session HP
Symposium H Poster Session

HP-1 Temperature Dependence of Nanocrystalline Aluminum Thin Film Elastic Constants by In-situ Brillouin Light Scattering and Picosecond Ultrasonics: Comparison to Molecular Dynamics*, **Philippe Djemia,*** LSPM-CNRS, France*; L Belliard,* INSP-UPMC, France*; H Zhang, Q Hu,* IMR-CAS, China*; F Challali, N Girodon-Boulandet, D Faurie,* LSPM-CNRS, France

We investigated the effective elastic constants in the temperature range [20°C, 600°C] of a polycrystalline aluminum thin film deposited on a silicon substrate by rf magnetron sputtering from Al target in Ar plasma discharge. From x-ray diffraction, Al polycrystalline film did not show strong crystallographic texture. The Brillouin light scattering (BLS) and the picosecond ultrasonics (PU) were complementary employed in combination with a furnace under high –vacuum (~10^{-5} mbar) or inert gas, to measure their acoustic and elastic properties. At room temperature, the Al film could be considered as nearly isotropic while increasing the temperature until 600 °C led to a continuous decrease of the elastic constants and an increase of the elastic anisotropy that was evaluated by a C_{11}/C_{33} ratio greater than one, of the in-plane (C_{11}) and out-of-plane (C_{33}) longitudinal effective elastic constants. Our results are found to be in a good agreement with previous experimental studies on bulk Al using standards ultrasounds equipment and our molecular dynamics theoretical estimates.

HP-2 High Resolution Full-field Curvature Measurement*, S Grachev,* ***Quentin Herault****, J Wang, I Gozhyk,* Saint-Gobain Recherche, France*; R Lazzari,* INSP-UPMC, France

A novel approach to curvature measurement will be presented. It allows for measuring curvatures below 10^{-7} m^{-1}. The method was successfully applied to observation of the first stages of growth of Ag by sputtering with unprecedented detail. The full-field capability allows for observation of complex forms resulting in variation of local curvature. The method was applied to a Mo film with inhomogeneous thickness distribution, which provided the curvature distribution maps. The poster will present the details of the method as well as its applications.

HP-4 In-situ High Temperature Characterization of DLC Films Using an Integrated Synchronized System*, M Rouhani,* National Chung Cheng University, Taiwan*; F Hong,* National Cheng Kung University, Taiwan*;* ***Yeau-Ren Jeng,*** National Chung Cheng University, Taiwan

An integrated synchronized system capable of mapping of depth-sensing indentation, spatially synchronized with a Raman spectrometer was applied to analyze microstructure, mechanical properties and surface roughness of DLC films over a specific area of the surface simultaneously. This integrated system was equipped with a high temperature chamber coupled with feedback control to make it possible to study the temperature effects on the mechanical properties and the microstructure evolution of the films, in ambient air up to 450̊C. A series of DLC films with different sp^3 content were deposited on Si substrates using filtered cathodic arc vacuum (FCVA) deposition system. Our study confirms the previous results that the thermal stability of the a-C films depends on their initial sp^3 content. The results show that the structural change is accompanied with profound increase in surface roughness of the films. The hardness of the films decreases with temperature increasing even before any changes in the microstructure of the films could be detected using Raman spectroscopy. The capability of the synchronized system enabled us to explore surface sensitive phenomenon of a-C film due to temperature rise that was not known before. Hence, our *in-situ* study showed for the first time that the surface sensitivity to temperature is greater than for the bulk of a-C films.

HP-6 Novel Methodology for the Evaluation of Mechanical Properties of Specific Crystalline Phases Present in Alumina Layers Formed by Plasma Electrolytic Oxidation (PEO) of Aluminium Alloys*, **Etienne Bousser,** A Yerokhin, A Gholinia, P Withers, A Matthews,* University of Manchester, UK

Aluminium alloys are widely used for their high specific strength but because of their lower hardness, these alloys often present a less than ideal resistance to surface wear. In order to improve the tribo-mechanical behaviour of these materials, electrolytic processes have been used for many years to promote the formation of protective oxide layers. More recently, Plasma Electrolytic Oxidation (PEO) has been shown to offer excellent wear performance through increased hardness due to the formation of hard crystalline phases during the oxide growth process at near-to-ambient bulk metal temperatures. However, the evaluation of the mechanical properties of the constituent phases in such oxide layers is difficult due to their complex microstructure. Indeed, these coatings are typically non-uniform with a shallow porous top layer which sits on a thicker, relatively dense layer comprising of a mixture of polycrystalline and amorphous oxide phases. In addition, complex multi-scale crack and pore networks are present over the entire thickness of the layer, making the evaluation of mechanical properties problematic using standard depth-sensing indentation methodologies. In this study, we present a novel approach for the precise evaluation of the mechanical properties of individual crystalline phases in the Al_2O_3 layers formed on aluminium alloys using Pulsed Bipolar PEO processes. The methodology presented in this poster is based on the statistical analysis of highly spatially-resolved mechanical property mapping of oxide layer cross-sections combined with high resolution characterization of the crystalline phases using Electron Back-Scattered Diffraction (EBSD). The EBSD was carried out on cross-sections prepared by Xe^+ ion Plasma FIB serial-sectioning and broad Ar^+ ion beam milling. In order to gain deeper insights into the processing effects on structure-property relationships, layers formed at different process times were evaluated.

HP-7 In situ High Temperature Fracture Toughness Evaluation of Hard Thin Ceramic Coatings by Means of a Micro-pillar Splitting Technique*, **Juri Wehrs,*** Platit AG, Switzerland*; J Best,* University of New South Wales, Australia*; M Polyakov, X Maeder,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; J Wheeler,* ETH Zürich, Switzerland*; M Morstein, B Torp,* Platit AG, Switzerland*; J Michler,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The fracture toughness at elevated temperatures is currently quite a difficult property to measure, but is a useful engineering variable for knowledge-based hard coating design. Most relevant applications of hard coatings, for example for metal cutting and forging tools, require usage at elevated temperatures. However several difficulties exist concerning toughness elucidation of small-scale specimens, mainly due to size effects, plasticity, residual stress effects and the influence of ion penetration from the sample fabrication process. Measuring at elevated temperatures magnifies the complexity of this task even further. Hence only few examples of high temperature fracture toughness measurements at high temperatures exist for small-scale samples.

In this study we explore the fracture toughness of a variety of arc-PVD coatings (CrN, AlTiN, AlCrTiN, and a AlCrN/SiNx nanocomposite) by means of a pillar splitting technique in the temperature range from RT to 500°C. The pillar splitting method for small-scale fracture toughness evaluation is inherently advantageous as the fracture event occurs under a sharp nanoindentation tip and in a region of material not significantly influenced from ion penetration and implantation. Therefore such a method is interesting for the study of brittle small-scale samples where ion implantation effects may be problematic. Further, unlike for other direct indentation techniques used to measure fracture toughness, the interface between coating and substrate does not interfere with the cracks that form, keeping the physics relatively simple.

Advanced Characterization Techniques for Coatings and Thin Films
Room Royal Palm 1-3 - Session H3

Characterization of Coatings in Harsh Environments

Moderators: JeffreyM. Wheeler, ETH Zürich, James Gibson, RWTH Aachen University

8:00am **H3-1 Zr/Nb Nano-multilayers – Structural and Mechanical Response to Radiation Damage***, M Callisti,* University of Cambridge, UK*;* ***Tomas Polcar****,* University of Southampton, UK

Zr/Nb nanoscale metallic multilayers (NMMs) with a periodicity (L) in the range 6 – 167 nm were prepared by magnetron sputtering studied by a combination of transmission electron microscopy analyses and nanomechanical measurements to reveal deformation and strengthening mechanisms. 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; plastic strain measured across compressed NMMs revealed a change in the plastic behaviour of α-Zr, which experienced a hard-to-soft transition. Multilayers were subject to high energy implantation (He, C, Si, Cu), gamma and proton irradiation, and the effects of radiation damage on mechanical properties were studied in detail. DFT simulations were used to identify helium diffusion and agglomeration in pristine and radiation-damaged Zr/Nb interfaces.

8:20am **H3-2 Nanoindentation of Commercial PVD Hard Coatings at Elevated Temperatures***, W Oliver,* Nanomechanics, Inc., USA*; M Romach,* Advanced Coating Service (ACS), USA*; R Anthony,* ***Kurt Johanns****,* Nanomechanics, Inc., USA

Ten different commercial PVD hard coatings have been characterized with nanoindentation experiments. The thickness of each film has been measured along with a pass/fail test for adhesion. The results from polished surfaces and the rougher as deposited surfaces have been compared. High-speed (NanoBlitz) experiments and statistical analysis have been used to understand the relationships between polished surface and as deposited results. The number of tests required to properly characterize the as deposited surface has been determined. In addition, a selection of the samples have been characterized with high speed, high temperature experiments. The hardness and modulus distributions at room temperature and high temperatures will be presented.

8:40am **H3-3 Elevated Temperature Micro-impact Testing of TiAlSiN Coatings***,* ***Ben Beake****, A Bird,* Micro Materials Ltd, UK*; L Arrom,* Cranfield University, UK*; F Jiang,* Huaqiao University, China

In developing advanced wear-resistant coatings for tribologically extreme highly loaded applications such as high speed metal cutting a critical requirement is to investigate their behaviour at elevated temperature since the cutting process generates frictional heat which can raise the temperature in the cutting zone to 700 °C or more. It has been shown previously that high temperature nanomechanical characterisation can be a valuable tool in understanding coating properties and how they will perform in different types of cutting tests with different requirements [1]. High temperature micro-tribological tests, such as micro-scratch and nano-impact extend the characterisation capability and have provided severe tests for coatings and correlate well to cutting tool life [2].

In this study we report the development of a novel micro-scale elevated temperature impact capability capable of producing repetitive impacts at significantly higher strain rate and energy than in the nano-impact test. With the new experimental test capability it is possible to study coating fatigue with less sharp spherical indenters than in the nano-impact test.

Micro-impact, nanoindentation and micro-scratch tests have been performed to 600 ºC on monolayer and nanolaminate TiAlSiN coatings on WC-Co. The key role of the elevated temperature nanomechanical properties in the impact behaviour of the coatings is discussed and correlations to elevated temperature micro-scratch tests to 600 ºC are investigated.

[1] *Progress in high temperature nanomechanical testing of coatings for optimising their performance in high speed machining*, B.D. Beake and G.S. Fox-Rabinovich, Surf. Coat. Technol. 255 (2014) 102.

[2] *Elevated temperature repetitive micro-scratch testing of AlCrN, TiAlN and AlTiN PVD coatings*, B.D. Beake, J.L. Endrino, C. Kimpton, G.S. Fox-Rabinovich and S.C. Veldhuis, International Journal of Refractory Metals and Hard Materials (2017).

9:00am **H3-4 Fracture Testing of Transition Metal (Oxy)Nitride Coatings***,* ***James Gibson****, S Rezaei, H Rueß, M Hans, D Music, O Hunold, S Wulfinghoff, J Schneider, S Reese, S Korte-Kerzel,* RWTH Aachen University, Germany

Transition metal (oxy)nitride coatings are used in polymer forming operations for a combination of outstanding wear resistance and chemical compatibility with the polymer materials. Varying the chemical composition and deposition parameters for the coatings will optimise mechanical properties by a combination of chemistry and microstructural optimisation. By developing a representative model for these materials, these materials can be rapidly and efficiently prototyped and improved. However, as both chemistry and microstructure play a role in the material properties, both of these variables must be taken account of in this model. This work demonstrates the first steps in linking quantum-mechanics, micro-mechanics, and meso-scale finite element models together in order to fully understand the behaviour of these coatings.

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 and titanium aluminium nitride and oxynitride 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 try and obtain plastic deformation in otherwise brittle coatings. Tests were carried out to 500˚C in-situ using a Nanomechanics inSEM system. Results are explained via DFT modelling of the coating chemistry, and integrated into a cohesive-zone element finite element model.

9:20am **H3-5 In-situ Study of Deformation and Fracture Processes in Nanostructured Metals at Elevated Temperatures***,* ***Daniel Kiener****,* Montanuniversität Leoben, Austria **INVITED**

Understanding the mechanical deformation and failure processes that take place in nanostructured bulk materials or for thin films on substrates is of prime importance for further improvement of the related material performance.

Miniaturized experiments provide the possibility to specifically test thin layers, individual phases, or interfaces, thereby extending our material understanding. In this presentation, recent developments using quantitative in-situ deformation testing and in-situ fracture experiments within scanning and transmission electron microscopes at ambient and elevated temperatures will be presented. The detailed observations accessible by such advanced experimental setups will be addressed in several case studies concerning the deformation and fracture behavior of, for example, nanostructured bcc metals and layered structures.

10:00am **H3-7 Cryogenic Micropillar Compression Transient Tests at the Lower Limit of Crystallinity Case Study: Nanocrystalline Palladium-Gold***,* ***Juri Wehrs****,* Platit AG, Switzerland*; J Schwiedrzik,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Deckarm,* Universität des Saarlandes, Germany*; J Wheeler,* ETH Zürich, Switzerland*; X Maeder,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; R Birringer,* Universität des Saarlandes, Germany*; J Michler,* 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 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 in a temperature interval from -55°C to 250°C. First we introduce and discuss the novel 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 **H3-8 Surface Roughness Effects of Hard Coatings under Three-body Abrasive Sliding Conditions***, **Reza Gheisari**, A Polycarpou,* Texas A&M University, USA

Three-body abrasive laboratory experiments were conducted using two different hard coatings intended for abrasive conditions for electrical submersible pumps (ESP) used in the oil and gas industry. The coatings used were specifically made for the above-mentioned application namely chromium carbide, and Diamonize coatings. These coatings have different surface topographies as well as different mechanical properties. Abrasive slurry of laboratory size-controlled silica sand in hydraulic oil was used to simulate the operational lubrication condition for the ESP. A specialized tribometer was used that simulated temperature, pressure, and velocity conditions encountered in ESPs and uses a pin-on-disk configuration, submerged in the slurry. In–situ measurements of the normal and friction forces were performed. A contact pressure of 6 MPa at a sliding velocity of 1.92 m/s was applied on the contact for 3×10^4 cycles, corresponding to 3500 meters. The focus of the study was to investigate the synergistic roles of the mechanical and roughness properties of the coatings on the wear and friction under three-body abrasive conditions. SEM and EDS analyses on the surfaces, as well as surface profilometry of the wear tracks were employed to gain more detailed perspective of the tribological mechanisms active at the macro and micro levels. It was concluded that while the effect of hardness ratio of the coating to the abrasive is righteously highlighted in previous studies, an RMS roughness close to 1 µm could significantly enhance the wear and friction performance of the coatings. In addition the ratio of abrasive size to surface roughness was proposed as an important factor to be taken into consideration while selecting the optimized coating for an abrasive condition.

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