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.

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