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

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