Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room Pacific Salon 1 - Session H3-2-WeA
Degradation under Extreme Conditions

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

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

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

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

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

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

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

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

Understanding the response of coatings and thin films to harsh and often superimposed extreme environments is important for materials selection and prediction of device performance lifetimes. In order to explore the response of materials in these extreme environments, Sandia National Labs is developing, as part of the Center for Integrated Nanotechnologies (CINT) user facility, an in-situ ion irradiation and nanomechanics scanning electron microscope (SEM). The facility being developed couples a JEOL IT300-HRLV SEM with a HVE 6 MV Tandem accelerator and a 1.2 kV KRI KDC10 gridded ion source. This large-chamber field emission SEM can obtain 1.5 nm resolution, while supporting large samples and high tilt capabilities. The SEM can be operated at a range of pressures (up to 650 Pa) and temperatures (up to 800 C). In-situ SEM ion irradiation is achieved with a 6 MV tandem with available beam species ranging from 800 keV protons to 100 MeV Au ions. Low energy ions can be introduced directly from the tandem ion sources at 46 keV or from the directly connected 1.2 kV ion source that can implant gaseous species at high flux and at energies ranging from 100 eV to 1.2 keV. There are three options for in-situ SEM nanomechanical testing (MTI Fullham heating-straining stage, Hysitron PI-85 nanoindenter, and the custom-built piezo fatigue tester) that significantly expand the range of mechanical properties that can be explored in the SEM. To aid rapid structure and composition analysis during in-situ experiments, the SEM is being outfitted with high speed CMOS based EBSD and large area SSD EDS system. Finally, to provide automated in-situ SEM experiments, a LabVIEW code is being refined that permits direct communication between the SEM, the accelerators, and the nanomechanical stages. To demonstrate these new capabilities, a range of initial experiments will be highlighted including, but not limited to: in-situ compression of additively manufactured (AM) miniature bear figurines, in-situ SEM fatigue in Pt and Pt-Au tensile bars, and in-situ irradiation degradation of an AM composite resulting from 20 MeV Au.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

4:40pm **H3-2-WeA-9 Small Scale Fracture of Mo_2BC Coatings**, ***Hariprasad Gopalan***, *R Soler, S Gleich, C Kirchlechner, C Scheu,* Max-Planck Institut für Eisenforschung, Germany*; J Schneider,* RWTH Aachen University, Germany*; G Dehm, V Arigela,* Max-Planck Institut für Eisenforschung, Germany

A density functional theory based approach was used to identify Mo_2BC as a promising candidate for hard coatings with improved fracture properties. A bipolar pulsed direct current magnetron sputtering system was used to deposit a 3 mm thick film on silicon from room temperature to 630°C. An additional thin film was synthesized on sapphire substrate at 900°C. The microstructure of the coatings characterized by transmission electron microscopy reveals that the degree of crystallinity increased with increasing deposition temperatures. The crystalline films possess a columnar morphology with nanocrystalline dimensions. The micro fracture behavior of the free standing coating was characterized by focused ion beam milled pre-notched microcantilever bending tests performed *in situ* in a scanning electron microscope. All cantilevers fractured after purely elastic loading. The fracture toughness of the coatings showed a weak dependence on the substrate deposition temperatures with a maximum of 5 MPa m$^{0.5}$. Fractography revealed the fracture path was either intergranular or through amorphous regions. Additional nanoindentation based fracture toughness estimates were obtained on the coating substrate system showing substantially higher toughness values. The disagreement between the nanoindentation and microcantilever bending experiments was rationalized in terms of a difference in the residual stress in the films which were characterized by wafer curvature measurements. Microfracture experiments in conjunction with nanoindentation revealed Mo_2BC coatings are excellent candidates as coating materials with high hardness and respectable fracture toughness confirming density functional theory studies.

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

This study investigated the effect of laser beam micromilling on the surface layer structure of HVOF sprayed WC-CoCr coating. The carbide layer was HVOF sprayed onto flat test samples made of austenitic stainless steel 1.4571 using the Thermico system and CJS K5.2-N gun. Ultra fine-grained WC-CoCr (84/12/4) powder, particle size 10 µm, was used for coat spraying application. The surfaces of test pieces were ground and polished after spraying. Then surface ablation was carried out by micromilling pre-set rectangular-shaped recesses with a nanosecond MOPA pulsed fiber laser. The experiment was planned using the Taguchi method (L9 3^3 orthogonal array). The process parameters examined were: laser power, pulse duration and laser beam scanning speed. Scanning Electron Microscopy / Energy Dispersive X-Ray Spectroscopy (SEM/EDS), X-ray Diffraction (XRD) phase analysis and 3D profilometry were used to evaluate structural changes. The effect of ablation process parameters (laser work parameters) on the treated coating surface condition, removed layer depth, surface roughness after the ablation process and treated coat phase composition was analysed. It was demonstrated that scanning speed reduction and laser pulse duration increase caused the increase of removed material layer thickness at a single beam pass. It was noted that laser treatment resulted in W_2C carbide formation on the treated WC-CoCr coating surface and molten material accumulated at the edges of the openings bored affecting their shapes and topography.

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