Tribology and Mechanical Behavior of Coatings and Engineered Surfaces
Room Town & Country B - Session E2-1-ThM
Mechanical Properties and Adhesion I

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Dr. Alice Lassnig**, Austrian Academy of Sciences, Austria, **Dr. Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

8:00am **E2-1-ThM-1 Residual Stress and Interfaces in Optical Coatings for Space Applications***, **Chelsea Appleget**, K. Folgner, V. Jiao, S. Dunscombe, S. Sitzman,* The Aerospace Corporation, USA*; D. White, A. Hodge,* University of Southern California, USA*; J. Barrie,* The Aerospace Corporation, USA **INVITED**

Optical coatings are an enabling technology in the space industry for a variety of applications requiring high reflectance, transmittance, spectral selectivity, or thermal control. Traditional multilayered optical coatings can be designed to achieve virtually any reflectance or transmittance characteristics by tuning layer thickness, material selection, and layer material properties. For space applications, additional multifunctional performance requirements must be considered, including, but not limited to, low residual stress, good durability and adhesion in extreme environments, and tuning of surface structure. The space environment brings increasing demands on the performance of optical coatings and materials, and as such, requires an understanding of the mechanisms leading to maximized multifunctional properties.

In this talk, a discussion on adhesion, stress, and interfaces for optical films for space applications will be presented, with two case studies for residual stress and mechanical properties to follow. The first study will explore multifunctional properties of antireflection (AR) coatings and evaluation of the structure-property relationship in the context of interface character and layer microstructure in crystalline/amorphous and amorphous/amorphous multilayers. Characterization by spectrophotometry, transmission electron microscopy, and nanoindentation showed substantial variations in microstructure and film properties with tuning of layer configurations for improved transmittance. The second case study presents microstructural tailoring in highly reflective, mirrored films for improved surface scatter and residual stress performance. Thick (>1 µm) optical coatings with favorable optical properties are desired in space to protect sensitive substrates, such as radiation sensitive glass. However, traditional high reflectivity optical films, such as Ag, exhibit a degradation in optical properties due to increases in surface roughness with increasing film thickness. To circumvent these traditional limitations, the role of alloying, microstructural progression, and in-situ and ex-situ residual stress evolution is explored.

In summary, the design and fabrication of multifunctional optical coatings for space requires insight into the role of residual stresses, interfaces, delamination behavior, and microstructure, all of which inform the process-structure-property relationship in optical films.

8:40am **E2-1-ThM-3 Increased Adhesion of Mo Films on Polyimide Through Interface Modification***, **Megan Cordill**, P. Kreiml,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; M. Rausch, C. Mitterer,* Dept. of Materials Science, Montanuniversität Leoben, Austria

Flexible and wearable electronics use metal films on polymer substrates. Here, the adhesion energy of these films to the substrates determines device performance. The interface between film and substrate is critical to adhesion energy. In this work, tensile induced delamination is used to quantify the adhesion energy of various Mo-based films on Polyimide, a common electrode material in thin film transistor displays. The method uses uniaxial straining to cause fracture of the film perpendicular and film delamination parallel to the tensile loading. Three different approaches to modify the interface to alter the adhesion energy will be compared, namely (i) the use of metallic interlayers between Mo and Polyimide (Al, Ta), (ii) the use of alloy interlayers between Mo and Polyimide (MoAl, MoTa), (iii) and the use of an alloyed Mo film (MoAl, MoTa) without an interlayer. Experiments on the different samples were performed with in-situ resistance measurements, confocal laser scanning microscopy (CLSM), and X-ray diffraction (XRD). CLSM allows for the quantification of crack density and delamination dimensions necessary for the adhesion measurement, while XRD provides film stress evolution to understand fracture and delamination mechanisms. The main aspects presented will be the adhesion energy along with the crack and stress evolution under uniaxial tensile loading. Results show that only the use of metallic interlayers between Mo and Polyimide (Al, Ta) provide a difference in the crack and delamination densities as well as a significant increase in the calculated adhesion energy compared to any of the other modification strategies.

9:00am **E2-1-ThM-4 Picosecond Acoustics as a Local and Quantitative Adhesion Technique***, **Arnaud DEVOS**, A. Vital-Juarez,* IEMN, France*; J. Desmarres,* CNES, France

The study of the bonding at interfaces between thin layers is of crucial importance in numerous applications whether they are related to optics, electronics or space exploration. A large number of methods have been developed to characterize the adhesion of a thin film to a substrate. But most of them are non local and destructive.

Acoustic waves are also sensitive to adhesion defects as they affect the way acoustic waves are reflected at the concerned interface. To address thin-films and complex stacks, ultra-high frequency acoustic waves (typ. greater than 10 Ghz) are needed. Such a range is only reachable to femtosecond laser techniques known as picosecond acoustics following the pioneer work of H. Maris in the 1980's. Recently we reported several studies that show how useful can be the picosecond acoustic technique to detect and quantify adhesion defects[1][2][3].

In this paper, we prepare dedicated samples to demonstrate the local character of the adhesion measurement by picosecond acoustics. For that a fingerprint is deposited between a silicon substrate and a thin metal film. A fingerprint acts as a large adhesion defect since the wafer surface is not clean at that place when the metal film is then deposited.

We then use the picosecond acoustic technique to map the reflection coefficient of ultrahigh frequency acoustic waves along the sample surface. A clear difference is first seen on and out the zone where the fingerprint has been deposited. Second, a high resolution mapping reveals the complete shape of the buried fingerprint: bumps and hollows of the fingerprint are easily discriminated acoustically as such details do not affect the adhesion in the same manner. The acoustic map reveals the fingerprint image and the guilty person can be identified !

References:

[1] A. Devos and P. Emery, “Thin-film adhesion characterization by Colored Picosecond Acoustics”, Surface and Coatings Technology 352, 406 (2018).

[2] A. Devos, A. Vital-Juarez, A. Chargui and M. Cordill, « Thin-film Adhesion: A Comparative Study Between Colored Picosecond Acoustics and Spontaneous Buckles Analysis”, Surface and Coatings Technology, 421, 127485 (2021).

[3] A. Vital-Juarez, L. Roffi, J.-M. Desmarres and A. Devos, « Picosecond Acoustics Versus Scotch Tape Adhesion Test: Confrontation on a Series of Similar Samples With a Variable Adhesion”, 448, 128926 (2022).

9:20am **E2-1-ThM-5 What Controls Size Effects on the Mechanical Properties of Additive Manufactured Polymers***, K. Shergill, Y. Chen, **Steve Bull**,* Newcastle University, UK

3D printed artefacts are becoming more common and the effect of printing parameters on their properties is key to their performance in applications. Although parameters like build orientation and raster direction are well-studied the effect of layer thickness (and its introduction of sizeeffects into the properties of the material) is less well-known. This study determines the influence of layer thickness on the mechanical properties of polylactic acid (PLA), acrylonitrile butadiene styrene (ABS) and PETG (Polyethlene terephtalate Glycol) 3D printed specimens made with fused filament fabrication (FFF). Samples were printed with differing layer thickness and tensile tested according to ASTM D638. The study also found that when increasing the layer thickness the mechanical properties of the specimens for both ABS and PLA decreased. When it came to ultimate tensile strength, the effect of layer thickness on PLA was more significant than on ABS with PETG being in between. The differences were attributed to differences in additive layer adhesion and the effect of the structure and defects introduced by the additive layerprocess.

9:40am **E2-1-ThM-6 Mechanical Properties and Microstructure Evaluation of HiPIMS Cu/W and Cu/Cr bilayers with Different Thickness Ratios**, ***Tra Anh Khoa Nguyen****, T. Zhang,* Graduate Institute of Precision Engineering, National Chung Hsing University, Taiwan*; H. Wang, H. Wu,* National Chung Hsing University, Taiwan*; M. Lin,* Graduate Institute of Precision Engineering, National Chung Hsing University, Taiwan

Copper/tungsten and copper/chromium bilayer films with a total thickness of 400 nm deposited using High Power Impulse Magnetron Sputtering(HiPIMS), have been compared with those fabricated by DC Magnetron Sputtering (DCMS). The different thickness ratios of 1:3, 3:5, 1:1, 5:3, 3:1 and sputtering power effects on the surface, microstructure, morphology, the texture of sputtered films, and mechanical properties of the bilayer thin films were investigated. The results show that the HiPIMS sputtered copper/tungsten and copper/chromium bilayers exhibit higher hardness, lower electrical resistance, and lower surface roughness than films deposited under the same deposition conditions as DCMS. These properties can be attributed to the increased peak power density of the target during the HiPIMS deposition process, which increases the ion energy and enables the deposition of highly dense grain structures and changes in texture transformation. Through the results of different thickness ratios, the deposition parameter database can be used for future HiPIMS copper/ tungsten and copper/chromium multilayer deposition.

10:00am **E2-1-ThM-7 Nanoengineered Thin Film Metallic Glasses with Mutual Combination of Large Yield Strength and Ductility**, *F. Bignoli,* CNRS, France*; A. Brognara, J. Best,* Max-Planck Institut für Eisenforschung GmbH, Germany*; P. Djemia, D. Faurie,* CNRS, France*; A. Li Bassi,* Politecnico di Milano, Italy*; G. Dehm,* Max-Planck Institut für Eisenforschung GmbH, Germany*;* ***Matteo Ghidelli,*** CNRS, France

Thin film metallic glasses (TFMGs) are object of intense research due to their a unique combination of mechanical properties involving large yield strength (~3 GPa) and ductility (>10%) [1]. Nevertheless, the synthesis of advanced TFMGs with engineered microstructure and the understanding of their mechanical properties are barely tackled. Here, I will present recent results involving two (2) strategies to develop nanoengineered TFMGs with a controlled microstructure down to the atomic scale, resulting in outstanding and tunable mechanical properties.

In the first case, I will show the potential of Pulsed Laser Deposition (PLD) as a novel technique to synthetize nanostructured $Zr_{50}Cu_{50}$ (%at.) TFMGs. I will show how the control of PLD process parameters enables to synthetize a variety of film microstructures among which compact fully amorphous and amorphous nanogranular, showing lower density and large free volume interfaces [2]. High-resolution TEM reveals a nano-laminated self-assembled atomic structure characterized by alternated layers with different chemical enrichment [2]. This results in an unique mechanical behavior as shown by in situ TEM/SEM tensile/compression tests, reporting homogeneous deformation for nanogranular (cluster assembled) TFMGs in combination with a large yield strength (>3 GPa) and ductility (>9 %) [2].

In the second case, I will focus on the fabrication of multilayers with nanoscale period alternating either fully amorphous or amorphous/crystalline sublayers. I will show how the control of the sublayer thickness (form 100 down to 5 nm) influences the deformation behavior affecting shear bands formation, while tuning the mechanical properties. As an example, alternating CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolayers results in an ultrahigh compressive yield strength (3.6 GPa) and large homogeneous deformation (~15%) [3]. Similarly, I will show the suppression of shear band/crack process in fully amorphous ($Zr_{24}Cu_{76}/Zr_{61}Cu_{39}$ %at.) multilayers with bilayer period < 50 nm, while keeping a mutual combination of large ductility (> 10%) and yields strength (>2.5 GPa).

Overall, our results pave the way to the development of novel amorphous materials with improved mechanical properties and wide application range especially in the field of microelectronics.

References:

[1] M. Ghidelli et al. Acta Mater., 131, 246, 2017.

[2] M. Ghidelli et al. Acta Mater., 213, 116955, 2021.

[3] G. Wu et al., Materials Today, 51, 6, 2021.

10:20am **E2-1-ThM-8 Measurements and Simulation of Mechanical Behavior of Amorphous and Crystalline Zr(–Hf)–Cu Thin-Film Alloys**, ***Stanislav Haviar****, T. Kozák,* University of West Bohemia, Czechia*; M. Meindlhumer,* Montanuniversität Leoben, Austria*; M. Zítek,* University of West Bohemia, Czechia*; J. Keckes,* Erich Schmid Institute of Materials Science, Austria*; P. Zeman,* University of West Bohemia, Czechia

Nanoindentation and microbending testing were used to investigate the mechanical properties of Zr(–Hf)–Cu thin-film alloys prepared by nonreactive magnetron co-sputtering. A detailed analysis of nanoindentation data and microscopic images of indents allowed a more precise determination of the effective Young's modulus of the films thanks to taking the pile-up effect into account.

Microbending testing in a scanning electron microscope was performed with microcantilevers fabricated by focused ion beam and the data were evaluated using a finite element method model. As outputs of this elasto-plastic model, Young's modulus, yield strength, elastic strain, apparent yield point and approximate ultimate strength and strain of the films were determined.

From a material point of view, the effect of elemental composition (Cu content and Hf substitution) and structure (glassy and crystalline) was investigated and discussed. It was shown that the substitution of Hf for Zr has less pronounced effect on the mechanical properties than the increase in the Cu content in the films that leads to a pronounced increase in the hardness, Young's modulus, elastic strain, yield strength, apparent yield point and ultimate strength but also to a decrease in the plastic parameter k and ultimate strain. Furthermore, a different atomic ordering in the crystalline and glassy Zr–Cu films of identical elemental composition results in differences in their mechanical properties and deformation behavior. The crystalline film was observed to be harder and stiffer with approximately the same elastic strain but higher yield strength and its plastic deformation was free of shear bands events.

[1] Haviar S., Kozák T. et al. Nanoindentation and microbending analyses of glassy and crystalline Zr(–Hf)–Cu thin-film alloys. *Surf. and Coat. Technol.* 399 (2020) doi: 10.1016/j.surfcoat.2020.126139

10:40am **E2-1-ThM-9 A Nanotwinned CoCrFeNi Medium Entropy Alloy with Ultrahigh Strength Over a Wide Range of Temperature**, ***Yun-Xuan Lin****, J. Wang, C. Tsai, S. Chang, F. Ouyang,* National Tsing Hua University, Taiwan

The medium-entropy alloys (MEAs) or high-entropy alloys (HEAs) have many superior properties, including high strength, high ductility, corrosion resistance, oxidation resistance, and high temperature resistance, which can be used in many applications. In addition, nanotwin (NT) structure plays an important role on strengthening mechanism in the microscopic scale because of its special properties, such as great thermal stability, high strain rate sensitivity, low electrical resistivity, and increased mechanical strength. In this study, we combined HEA and nanotwin structure to fabricate NT-MEA thin films and investigated its mechanical properties at different temperature ranges. At first, the NT CoCrFeNi MEA films were fabricated by pulsed DC magnetron sputtering system on Si substrate. The hardness of nanotwinned CoCrFeNi medium entropy alloy films was examined by nanoindentation at varied temperatures from -80 ℃ to 300 ℃. At the same time, the microstructures of the indentation regions were studied by transmission electron microscope (TEM). As-deposited CoCrFeNi medium entropy alloys had a columnar grain structure containing high-density nanoscale growth twins parallel to the substrate with an average twin thickness of 2.4 nm. The results show that NT-MEA was observed to have remarkably high strength, outperforming many other bulk HEAs, MEAs, nanocrystalline HEAs, and conventional NT-metals in the temperature range from -80 °C to 300 °C. The maximum hardness of NT-MEA was measured with a value of 11.3 GPa at cryogenic environment of -80°C and its hardness slightly decreased to 9.4 GPa when temperature increased from -80 ℃ to 300 ℃. Meanwhile, neither cracks nor fractures were observed in all temperatures, suggesting that the NT-MEA was still ductile material, especially in the cryogenic environment. The corresponding deformation mechanism at different temperature ranges would be discussed in details in this talk.

11:00am **E2-1-ThM-10 Material Properties and Mechanics of Eggshells—Nature's Survival Capsules***, **Jia-Yang Juang,*** National Taiwan University, Taiwan **INVITED**

Amniotic eggs emerged over 300 million years ago in tetrapod vertebrates and are now the primary reproductive mode of all terrestrial amniotes. Unlike the simpler, shell-less eggs of amphibians, amniotic eggs are covered with shells, which allow the eggs to develop fully on land without drying out and thus open up new terrestrial habitats for amniotes, including birds and egg-laying reptiles. In birds, eggshells are multifunctional thin-walled structures that protect the embryo from excessive water loss, provide calcium, and sustain the weight of incubating birds. As a load-bearing structure, the eggshell must be strong enough to resist deformation and impact. Meanwhile, it must be breakable for the hatchling to emerge. Those are mechanical design trade-offs that must be adequately balanced. Here, we use combined experimental, numerical, and theoretical methods to analyze the morphology, material properties, and mechanics of 700 freshly-laid bird eggs from 58 species across three orders of magnitude in egg mass (from 1 g to 1459 g). We characterize the mineral content by acid-base titration, the crystallographic characteristics by electron backscatter diffraction (EBSD), and effective Young's modulus E by compression test and finite-element analysis (FEA). We find that the mineral content is positively correlated with E, with the lowest of 83.1% and 23.28 GPa in Zebra finch and the highest of 96.5% and 47.76 GPa in ostrich in this study. The EBSD shows that eggshell is anisotropic and non-homogeneous, with different species exhibiting different degrees of crystal orientation and texture. The experimental results are consistent with the nanoindentation test and theoretical prediction of linear elasticity. This study provides new data and insights into the material properties and mechanics of eggshells and provides clues for the future development of bioinspired multifunctional thin-walled shells.

11:40am **E2-1-ThM-12 Effects of Cathodic Currents on Mechanical and Corrosion Behaviors of Plasma Electrolytic Oxidation Coatings on 6061 Aluminum Alloy***, C. Tseng,* Department of Materials Engineering, Ming Chi University of Technology. Center for Plasma and Thin Film Technologies, Ming Chi University of Technology, Taiwan*; **Xianghe Wang,*** Department of Materials Engineering, Ming Chi University of Technology, Taiwan

In this study, we fabricated the porous aluminum oxide (Al_2O_3) coatings on 6061 aluminum alloy by using plasma electrolytic oxidation (PEO) in alkaline sodium silicate solution under bipolar pulsed power mode with maxima anodic voltage at 500V, maxima cathodic voltage at 100V, duty cycle of 25%, pulse frequency in 1000 Hz, anodic current in 2A and cathodic current in 1~5A.The effects of cathodic current on microstructural, mechanical and corrosion behaviors of PEO coatings on 6061 aluminum alloy were investigated by X-ray diffractometer (XRD), scanning electron microscope (SEM), energy-dispersive X-ray spectroscopy (EDS), scratch test, pin-on-disk wear test and potentiodynamic polarization measurement. The XRD results show that the PEO coatings are mainly composed of a-Al_2O_3 and γ-Al_2O_3. However, the ratios of a-Al_2O_3 and γ-Al_2O_3 in PEO coatings are identical with various cathodic currents applied. The SEM images display that the thickness of PEO coating is increased with increasing cathodic current from 11mm (1A) to 17mm (5A) and surface porosity of PEO coating is decreased with increasing cathodic current from 16.2% (1A) to 9.4% (5A). The potentiodynamic polarization curves show that the PEO coatings, as compared to 6061 aluminum alloy, exhibit higher corrosion resistances in 3.5 wt% NaCl solution. However, the corrosion current density (Icorr) and passivation current density (Ipass) for PEO coatings are decreasing with increasing cathodic current applied. In summary, the thickness, porosity and corrosion resistance of PEO coatings on 6061 aluminum alloy can be significantly improved by controlling cathodic current applied.

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