Tribology and Mechanics of Coatings and Surfaces
Room Town & Country B - Session MC2-1-TuA

Mechanical Properties and Adhesion I

Moderators: Jazmin Duarte, MPI für Eisenforschung GMBH, Germany, **Bo-Shiuan Li**, National Sun-Yat Sen University, Taiwan

1:40pm **MC2-1-TuA-1 Boosting Mechanical Properties of Metallic Thin Films Through Advanced Nanoengineered Design Strategies**, *B. Francesco,* LSPM-CNRS, France*; A. Brognara,* Max-Planck-Institut für Eisenforschung, Germany*; P. Djemia, D. Faurie,* LSPM-CNRS, France*; A. Li Bassi,* Politecnico di Milano, Italy*; G. Dehm,* Max-Planck-Institut für Eisenforschung, Germany*; **Matteo Ghidelli (matteo.ghidelli@lspm.cnrs.fr),*** Laboratoire des Sciences des Procédés et des Matériaux (LSPM), CNRS, France **INVITED**

The current trend toward miniaturization in devices components in key technologies such as micro-/nanoelectronics, energy production, sensors and wear protection requires the development of high-performance nanostructured films with superior mechanical properties. Especially, mutually excluding structural properties such as high yield strength and ductility need to be combined, but also high adhesion with the substrate and large fatigue resistance. In order to trigger microstructure-induced material properties, control of the micro-scale structure, atomic composition, average grain size, and layer/film thickness must be optimized based on nanoengineering design concepts.

Here, I will present recent results for several class of advanced thin film materials including nanostructured metallic glasses (ZrCu/O, ZrCuAl/O...)[1-3] high entropy alloys (CoCuCrFeNi, Al/CoCuCrFeNi) and nanolaminates (fully amorphous, amorphous/crystalline)[4], showing how the control of micro-structure affect the and micro-scale mechanical behavior and enable ultimate mechanical properties.

Among the main results, I will show the potential of Pulsed Laser Deposition (PLD)[1, 2] as a novel technique to synthetize nanostructured cluster-assembled ZrCu, ZrCuAl/O, and CoCuCrFeNi films, reaching ultimate yield strength (>4 GPa) and ductility (>15 %) for ZrCuAl/O films. I will show how the control of the sublayer thickness (from 100 down to 5 nm) in fully amorphous nanolaminates influences the deformation behavior suppressing the shear bands formation, while tuning the mechanical properties with mutual combination of large ductility (> 10%) and yields strength (>2.5 GPa). Finally, I will show how alternating CrCoNi (crystalline)/TiZrNbHf (amorphous) nanolayers results in an high compressive yield strength (3.6 GPa) and large homogeneous deformation (~15%)[4].

Overall, our results pave the way to the development of nanostructured thin films with boosted mechanical properties and wide application range.

References:
[1] M. Ghidelli et. al., *Novel class of nanostructured metallic glass films with superior and tunable mechanical properties*, Acta Mater. **213** (2021) 116955.
[2] C. Poltronieri et al., *Mechanical properties and thermal stability of ZrCuAlx thin film metallic glasses: Experiments and first-principle calculations*, Acta Mater. **258** (2023) 119226.
[3] A. Brognara, et al., *Effect of composition and nanostructure on the mechanical properties and thermal stability of Zr100-xCux thin film metallic glasses*, Mater. Design **219** (2022) 110752.
[4] G. Wu et al., *Symbiotic crystal-glass alloys via dynamic chemical partitioning*, Mater. Today **51** (2021) 6-14.

2:20pm **MC2-1-TuA-3 The Evolution of Residual Stress in the Immiscible Cr-W Alloy System**, ***Tong Su (tong_su@brown.edu)***, Brown University, USA*; J. Robinson, G. Thompson,* University of Alabama, USA*; E. Chason,* Brown University, USA

Metal alloy films are used in numerous technical applications such as magnetic storage, catalysis and hard coatings. As with any coating, residual stress is critical to their adhesion and physical properties. While there have been numerous studies of residual stress evolution in elemental metal systems under different processing conditions with corresponding mechanisms, there are far fewer in alloys.Such studies have been indispensable to understand adatoms evolution and residual stress development. In this work we study the stress in Cr-W which is a continuation of work performed in the Mo-V and W-V systems. These alloys are BCC elements that exhibit a miscibility gap which thermodynamically drive the elements to partition from the other. The measurements were performed at several deposition rates from 0.8 nm/s to 6.0 nm/s and pressures of 0.27 Pa and 0.47 Pa with the stress measured by an in-situ wafer curvature measurement technique. While thermodynamically driven to partition, the results indicate that alloy stress can be explained with similar mechanisms invoked for elemental systems. Nevertheless, the kinetic parameters that control the stress are a complicated superposition of the effects of the single elemental components.

2:40pm **MC2-1-TuA-4 Adhesion and Friction-wear Characterization of W-doped Hydrogenated Diamond-like Carbon (a-C:H) Coatings**, ***Ihsan Efeoglu (iefeoglu@atauni.edu.tr)***, *Y. Totik, G. Gulten, B. Yaylali, M. Yesilyurt,* Atatürk University, Turkey*; R. Gunay, G. Kara, B. Altintas,* TUSAS ENGINE INDUSTRIES (TEI), Turkey

AISI 4130 alloy steel, a significant material type for the majority of engineering applications in the industry, is used extensively in the aerospace, automotive, and defense industries due to its crucial characteristics, including high strength, durability, machinability, and corrosion resistance. Enhancing this material's surfaces mechanical and tribological characteristics with Tungsten (W)-doped diamond-like carbon (DLC) coatings stands out as a way to improve its performance in this investigation. Amorphous hydrogenated diamond-like carbon (a-C:H) coating has great mechanical and tribological properties. In this study, W-doped DLC coatings have been deposited on AISI 4130 via closed-field unbalanced magnetron sputtering. A L9 orthogonal array of the Taguchi method was utilized to optimize the variable coating parameters applied in the magnetron sputtering process. The microstructure, thickness, and composition of the a-C:H:W coatings were examined using scanning electron microscopy. The crystallographic characteristics of coatings were evaluated using X-ray diffraction in order to provide an extensive understanding of the coating structure. The specific measurements of the hardness and elasticities of the coatings were obtained using the nanoindentation test. The scratch test method was used to examine the adhesion properties of the coatings by determining their critical load values at which film delamination occurred. The tribological behavior of uncoated AISI 4130 substrate and a-C:H:W coating was determined with a pin-on-disc tribometer against an Al_2O_3 ball under dry sliding conditions. Delamination and gradual failures occurring in the wear test of the uncoated specimen increased the friction coefficient. On the contrary, the a-C:H:W coating exhibits such superior tribological properties that the friction coefficient decreased due to the prevention of delamination and gradual failures to a certain extent. It was observed that the scratch-adhesion properties of the coated specimens significantly contributed to the improvement of tribological performance.

3:00pm **MC2-1-TuA-5 Numerical and Experimental Evaluation of Cyclic Contact Loads on Titanium Borides**, *A. MENESES AMADOR, G. RODRIGUEZ CASTRO, **Hugo Alberto Pérez Terán (hap_ter@hotmail.com)**, M. Melo-Pérez,* Instituto Politécnico Nacional, Mexico

In this work, an experimental and numerical study of the contact fatigue test on titanium boride (TiB_2/TiB) coatings is presented. The boride layers were formed at the surface of Ti6Al4V alloy using the powder-pack boriding process at temperatures of 1050 °C for10, 15 and 20 h of exposure times in order to obtain three different thicknesses. Optical microscopy was used to characterize the boride layer, the results showed an outer TiB_2 layer and an inner TiB layer (whiskers). The mechanical characterization (hardness and Young's modulus) was carried out using Berkovich instrumented indentation technique. From the set of experimental conditions of the boriding process, cyclic contact loads were applied with a MTS Acumen equipment by repetitive impact of a sphere on the layer-substrate system. The experimental methodology consisted first determining the critical static load (load magnitude where cracks are observed) afterward cyclic sub-critical loads are applied with a frequency of 6 Hz for the three coatings. The test results indicate that the thinner coating exhibited better behavior under cyclic contact loads while thicker thickness showed greater damage under similar conditions. In order to evaluate the stress field generated in the boride layer during the application of static and dynamic loads, numerical simulations based in the finite element method were developed. The results showed good approximations with regard to contact diameters and residual depths obtained experimentally.

4:00pm **MC2-1-TuA-8 Mechanical Characterization of Nb-doped MoS_2 Coatings Deposited on H13 Tool Steel using Nb-based Interlayers**, ***Miguel Rubira Danelon (miguel.danelon@usp.br)**, N. Kyioshi Fukumasu,* University of São Paulo, Brazil*; A. Alves Carvalho,* Aeronautic Institute of Technology, Brazil*; R. Rodrigo Rego,* Aeronautics Institute of Technology, Brazil*; I. Fernanda Machado, R. Martins de Souza, A. Paulo Tschiptschin,* University of São Paulo, Brazil

Molybdenum disulfide is a 2D material with excellent lubricant properties, attributed to a low coefficient of friction (COF) resulting from weak Van der Waals forces between lattice layers and shear-induced crystal orientation. However, film oxidation harms its efficacy in humid atmospheres, leading to an increased COF and poor surface adhesion, making its use preferable in dry or vacuum conditions. To overcome these challenges, doping MoS_2 with elements, such as Nb, Ti, C, and N, emerges as a promising solution. Doping alters the reactions between the film and environmental oxygen atoms, reducing the environmental sensitivity of the film. Literature reports that doping MoS_2 with Nb promotes the formation of NbS_2 phases, which exhibit superior oxygen-trapping capabilities compared to conventional MoS_2 films, increasing its performance in humid conditions. Nevertheless, the adhesion of these coatings to a steel substrate present challenges and strategies involve the reduction of residual stresses and increase chemical affinity to the substrate by using of niobium-based materials as interlayer. Different interlayer characteristics, such as hardness, thickness and composition, can influence adhesion. A metallic niobium interlayer enhances film adhesion but, alternatively, a NbN interlayer, with ceramic characteristics, such as higher hardness, further improves adhesion. In this study, Nb-doped MoS_2 films were deposited on H13 steel using the pulsed direct current balanced magnetron sputtering technique. Different niobium-based interlayers were deposited to evaluate tribological behavior and adhesion properties of Nb-doped MoS_2 coatings. Scratch tests, conducted at room temperature and humidity, without lubrication, and under a progressive load, were performed to analyze the COF and adhesion of the coating, while instrumented indentation tests were conducted to assess the hardness and elastic modulus of the coatings. The Nb concentration of the films and interlayer was evaluated using scanning electron microscopy (SEM) with Energy-dispersive X-ray spectroscopy (EDS). Results indicated that a thicker interlayer optimally promoted the adhesion of the film, together with a high concentration of Nb on the interface between the Nb-doped MoS_2 film and the niobium-based interlayer. This result is justified by the increase of hardness led by higher Nb concentrations. Furthermore, better adhesion of the film promoted a low COF at greater load during tests. In summary, niobium-based materials can be used to enhance the adhesion properties of Nb-doped MoS_2 films and consequently improve their performance.

4:20pm **MC2-1-TuA-9 Mechanical Properties and Adhesion of Al Thin Films with Al_2O_3 Interlayers on Flexible Substrates**, ***Johanna Byloff (johanna.byloff@empa.ch)**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; P. Renault,* University of Poitiers, France*; D. Faurie,* Université Paris-Saclay, France*; S. Husain,* University of Poitiers, France*; D. Casari, T. Edwards, B. Putz,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland

Metal thin films on polymers serve a variety of applications in the packaging, flexible electronics, and space sector. Challenges include mechanical failure during use, material restrictions, and non-recyclability. In the Aluminium (Al)-Polyimide (PI) system, favorable adhesive properties are attributed to an amorphous Al-O-C interlayer [1-3] (IL, 5 nm thick) between the metal film and the PI substrate. Through a combined atomic layer (ALD) and physical vapor deposition (PVD) setup, we are uniquely able to mimic interlayers artificially over a wide thickness range to study their mechanical and interfacial benefits. Using this setup, Al thin films (150 nm) with different Al_2O_3 interlayer thicknesses (0, 0.12, 1, 5, and 25 nm) were deposited on a polyimide substrate. These bi-layer samples were subjected to equi-biaxial tensile loading [4] with in-situ X-ray diffraction and electrical resistivity measurements at Synchrotron SOLEIL. The evolution of Al film stress, width of the Al diffraction peak and electrical resistivity could be determined as a function of IL thickness and applied strain. The Al and oxide layer thickness and microstructure as well as crack density and spacing after testing were investigated using scanning and transmission electron microcopy. Our results reveal a positive influence of the preceding ALD step on the mechanical properties of the Al thin films. All films with artificial ALD interlayers show reduced roughness and grain width in their PVD sputtered Al layers, resulting in a higher 0.2% yield stress, while overall maintaining ductile electro-mechanical behavior. This is possibly due to modifications of the PI substrate surface through ALD. Significant embrittlement was observed only in the Al film with 25 nm interlayer thickness. Most notably, comparison of a 5 nm artificial and natural interlayer shows a similar resistivity but a two-fold increase in yield strength in the artificial case. Adhesion between metal film and polymer substrate was evaluated with the tensile induced delamination method, indicating better adhesion (lower buckle density) with artificial Al_2O_3 interlayers.

[1] B. Putz et al., Surf. Coat. Technol. 332, 368 (2017)

[2] S. H. Oh et al., Scr. Mater. 65, 456 (2011)

[3] L. Atanasoska et al., J. Vac. Sci. Technol. A 5, 3325 (1987)

[4] G. Geandier et al., Rev. Sci. Instrum. 81, 103903 (2010)

4:40pm **MC2-1-TuA-10 Buckling Structures, a Relevant Signature of the Mechanical Properties of Film/Substrate Systems**, ***Christophe COUPEAU (christophe.coupeau@univ-poitiers.fr)**,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France*; G. PARRY,* SIMAP, Grenoble-INP, CNRS, France*; J. DURINCK,* Institut Pprime - CNRS - ENSMA - Université de Poitiers, France

Thin films and coatings are used in a wide range of technological applications, such as microelectronics, packaging or optics. They often develop high residual stresses during the deposition process, sometimes about few GPa in compression. Such large compressive stresses may cause the nucleation and growth of buckling structures that generally result in the loss of functional properties that were initially conferred to such film/substrate composites. The aim of our studies is consequently to have a better understanding of the buckling phenomenon, by identifying the relevant parameters to prevent, to limit, or to control its occurrence.

From an experimental point of view, the fine investigation by optical and atomic force microscopies of the morphology of elementary buckling structures is consequently of great interest in order to qualitatively, or even quantitatively, extract some mechanical parameters of the film/substrate systems. Our studies concern for instance the effect of both elasticity [1-3] and plasticity [4] of the substrates on the maximum deflection of the buckles, the question of vacuum below the buckling structures [5], the effect of a pressure mismatch between the buckled film and its substrate on the occurrence of specific structures (such as donut-like or flower-like buckles) [6,7], the limit of the elastic theory framework to understand the buckling when plasticity is taking place in the film [8].

[1] G. Parry *et al*., *Physical Review E* 74 (2006) 066601.

[2] G. Parry *et al.*, *Acta Materialia* 52 (2004) 3959.

[3] R. Boijoux *et al.*, *Thin Solid Films* 645 (2018) 379.

[4] F. Foucher *et al*., *Phys. Rev. Lett*. 97 (2006) 096101.

[5] C. Coupeau *et al.*, *Thin Solid Films* 518 (2010) 5233.

[6] S. Hamade *et al*., *Phys. Rev. E* 91 (2015) 012410.

[7] S.-J. Yu *et al*., *Int. J. of Solids and Struct.* 225 (2021) 111053.

[8] K. Heng Meng *et al*., *submitted to Surface and Coating Technology*

Author Index

Bold page numbers indicate presenter