Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM2-1-MoA

Advanced Mechanical Testing of Surfaces, Thin Films, Coatings and Small Volumes I

Moderators: Thomas Edwards, Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland, **Olivier Pierron**, Georgia Institute of Technology, USA

1:40pm **CM2-1-MoA-1 Micromechanics During Hydrogen Charging and the Study of Hydrogen Barrier Coatings***, **Maria Jazmin Duarte (j.duarte@mpie.de)**, H. Gopalan, J. Rao, C. Scheu, G. Dehm,* Max-Planck Institut für Eisenforschung GmbH, Germany **INVITED**

Understanding the effects of hydrogen in materials became a pressing topic with the imminent shift towards green technologies, and the use of hydrogen as energy carrier. It is expected that the use of hydrogen will increase in all industries, together with the need for safe transport and storage and consequently the development of new materials and technologies to cope with it. A critical challenge is hydrogen-induced damage, or hydrogen embrittlement, that can cause the sudden failure materials. Hydrogen barrier coatings represent, in this regard, an appealing option to prevent and/or slow down the hydrogen ingress into structural alloys that are susceptible to embrittlement.

To characterize hydrogen and its effects in materials, at the relevant small-scale dimensions where embrittlement initiates, is a substantial yet demanding task. Current studies on hydrogen effects are in their majority limited to post-mortem probes and ex-situ charging, which neglect diffusible hydrogen, its migration and desorption at the analysis time. To rise above these constraints, we designed a novel “back-side” charging approach, to perform micromechanical testing during hydrogen charging [1]. Hydrogen is generated electrochemically at the back-side and diffuses towards the testing (front-side) surface. This unique method allows differentiating between the effects of trapped and mobile hydrogen, and performing well controlled measurements with different hydrogen levels monitored over time to consider hydrogen absorption, diffusion and release.

Using this new method, we unraveled dynamic effects of hydrogen on the mechanical properties of bulk alloys [2], and recently, we successfully applied it to study of hydrogen barrier coatings [3,4]. In this talk, I will present an overview of the technique, together with the case study of an Al_2O_3 hydrogen barrier coating. The hydrogen diffusion on Al_2O_3, ~9 orders of magnitude slower with respect to the used substrate, was measured by Kelvin probe. The mechanical stability of the coating was tested by nanoindentation and nanoscratching during hydrogen loading. The accumulation of hydrogen at the substrate-coating interface reduces the critical load required for cracking and leads to local delamination. Mechanical tests were complemented by atom probe tomography, confirming the presence of hydrogen close to the substrate/coating interface, and transmission electron microscopy, revealing the underlying microstructural changes.

[1] M.J. Duarte, et al., J. Mat. Sci. 56 (2021) 8732.

[2] J. Rao, et al., Mater. Des. 232 (2023) 112143.

[3] M. Wetegrove, et al., Hydrogen 4(2) (2023) 307.

[4] S.W Hieke, et al., Adv. Eng. Mater. (2023), *Accepted*.

2:20pm **CM2-1-MoA-3 The Micromechanical Behavior of Magnetron Sputtered TiN/Nb Multilayers***, S. Kagerer, N. Koutná,* Institute of Materials Science and Technology, TU Wien, Austria*; L. Zauner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wójcik,* Institute of Materials Science and Technology, TU Wien, Austria*; G. Habler,* Department of Lithospheric Research, University of Vienna, Austria*; P. Polcik, S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; O. Hunold,* Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; **Rainer Hahn (rainer.hahn@tuwien.ac.at)**,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Damage tolerance is a prerequisite for using protective coatings in components subject to long-term stress. Physical Vapor Deposition offers possibilities in coating architectures using combinations of ductile and hard materials, even on the nm scale. However, ductility through dislocation motion is often suppressed on the micro-scale due to geometric limitations, resulting in unusually brittle behavior. In this work, we show a linear dependence between the necessary shear stress for dislocation motion in Nb layers and the overall plastic behavior of micropillar samples.

Computational pre-screening identifies fcc-TiN/bcc-Nb as a promising system providing stable, sharp, and strong interfaces with essentially different elastic moduli. Using a TiN compound target enables a sharp interface without nitrogen cross-contamination. Layer variation and changing the TiN to Nb ratio offer insights into the small-scale plastic behavior using the micropillar compression test. These show a fluent transition from ductile deformation for thick Nb layers to a brittle behavior similar to monolithic TiN upon decreasing the Nb layer thickness.

Combining micromechanical data with TEM analysis of fractured micropillars, we correlate these observations with increased stresses necessary for dislocation motion within the confined layer slip model. Furthermore, we will show the results of unique experiments combining micromechanics with synchrotron nanodiffraction to understand the stress situation in a pillar and describe deformation mechanisms.

2:40pm **CM2-1-MoA-4 Deformation Behaviour and Plasticity in FCC-BCC High Entropy Alloy Nanolaminate Structures***, S. Tsianikas,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Thun, Switzerland*; C. Tian,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; C. Guerra-Nuñez,* Swiss Cluster AG, Thun, Switzerland*; J. Michler, X. Maeder, **Amit Sharma (amit.sharma@empa.ch)**,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland

In recent years, metal multilayer composites have been the focus of research due to their exceptional mechanical properties. Recent experimental [1-3], theoretical, and modeling [4]studies on multilayers have indicated that the enhancement of both strength and ductility is related both to the structure and properties of the interfaces between the layers, as well as the thicknesses and properties of the individual layers [5]. In spite of the ample literature available on pure metallic nanolaminate structures, the experimental data on compositionally complex alloy multilayers is rather missing.

In this context, here we present recent experimental data on the fabrication and mechanical behavior of nanolaminate FCC-BCC high entropy alloy thin films with interlayer thicknesses 50 nm. The alternating FCC-BCC layers are separated by atomic layer deposition of 2 nm amorphous Al2O3 layer without breaking the vacuumin a new Cluster System combining both ALD and PVD in the same equipment (Swiss Cluster AG). As a model system, FCC-NiCoCrFe and BCC- NiCoCrFe-Al (with Al ~10 at. %) layers with a total thickness of 3 microns is deposited on Si (100) substrate by magnetron sputtering and subsequently tested by micro compression and nanoindentation experiments. The mechanical response of the multi-layered structures is also compared with FCC-BCC multilayer without ALD and single-layer FCC and BCC counterparts. The uniformity in composition and microstructure of interlayers is confirmed by performing S/TEM imaging along the cross-section samples prepared by FIB using a standard liftout procedure. The microcompression experimental results on micro-pillars show a clear effect of interfaces and interlayer size effect on the mechanical response of nanolaminates at different strain rates. The post-mortem electron microscopy investigation provides insight into deformation mechanisms and deformation-induced phase transformations in the individual layers. This first study on multilayer film of two HEA’s will help fundamental studies on high entropy alloys and transformative to other complex systems.

1. S.J. Zheng, I.J. Beyerlein, J. Wang, J.S. Carpenter, W.Z. Han, N.A. Mara, Acta Materialia, 60 (2012) 5858-5866.

2. N.A. Mara, I.J. Beyerlein, J.S. Carpenter, J. Wang, JOM, 64 (2012) 1218-1226.

3. N. Li, N.A. Mara, J. Wang, P. Dickerson, J.Y. Huang, A. Misra, Scripta Materialia, 67 (2012) 479-482.

4. J. Wang, K. Kang, R.F. Zhang, S.J. Zheng, I.J. Beyerlein, N.A. Mara, JOM, 64 (2012) 1208-1217.

5. N. Mara, I. Beyerlein, J Mater Sci, 49 (2014) 6497-6516.

3:00pm **CM2-1-MoA-5 Characterisation of Hydrogen in Coatings and Thin Films Using Atom Probe and TDMS***, **Peter Felfer (peter.felfer@fau.de)**,* Friedrich-Alexander University, Germany **INVITED**

In the transition to hydrogen as a future energy vector, thin films and coatings play a crucial role. Prominent current applications are coatings for bipolar plates in fuel cells and electrolyzers. In the future, many more applications are likely, such as diffusion barrier and hard coatings on high-strength or wear exposed components such as valves and hydrogen injectors. This is because many base materials of hard coatings have very low hydrogen diffusion coefficients. However, real hard coatings are not single crystals and thus a much better understanding of the interaction of hydrogen with real hard coatings is required. Especially interactions between hydrogen and crystal defects are important as they carry permeation and trigger failures.

To understand these interactions, we are developing new nanoscale characterisation methods. These include the development of an special atom probe with ultra-low hydrogen background for nanoscale imaging and a similar thermal desorption system for analysis of mobile and trapped hydrogen. Both of these systems are based on titanium ultra-high vacuum chambers, drastically reducing the amount of background hydrogen in the vacuum. As a result, very little to no spurious hydrogen appears in the analyses. For the titanium atom probe, this has been demonstrated in voltage pulsing already. This method of analysis is however not suitable for coatings. A laser for the analysis of non-conductive materials such as thin films and coatings is currently being fitted. This unlocks the ability to quantitatively image hydrogen in thin films at the nanoscale and thus shed light on the prermeation mechanisms and interactions with crystal defects. First results will be shown in the talk. In parallel, we are testing the titanium thermal desorption system on thin films, to complement the nanoscale imaging of the atom probe with qualitative and eventually quantitative results on the amounts of mobile and trapped hydrogen in thin films.

4:00pm **CM2-1-MoA-8 Analysis of Stress Field in Nickel Borides Layer Produced by Vickers Indentation Tests in Cross Section: Finite Element Method***, **T. N. Cabrera-Yacuta (tcabreray1800@alumno.ipn.mx)**, G. Rodríguez-Castro, A. Meneses-Amador, I. Arzate-Vázquez,* Instituto Politécnico Nacional, Mexico*; O. Morales-Contreras,* Universidad Autónoma de Baja California, Mexico*; I. Campos-Silva, M. Melo-Pérez,* Instituto Politécnico Nacional, Mexico

This research studies numerically the stress fields formed in layers of nickel borides generated by Vickers indentations in cross section at different distances from the layer/substrate interface. Three powder-pack boriding conditions at 850, 900 and 950 °C for 2, 4 and 6 h, respectively, were applied to Inconel 718 for the formation of nickel borides. By means of X-ray diffraction, the Ni_4B_3, Ni_2B, Ni_3B phases were identified. In addition, a hardness range between 23.8 and 26 GPa was determined by Berkovich instrumented indentation, while 280 to 380 GPa for Young's modulus. The stress fields were analyzed by the finite element method using an explicit dynamic analysis. The numerical model is constituted by a Vickers indenter as a discrete and rigid body and by a 3D deformable solid defined through sections. As the layer thickness increases, the system is less sensitive to applied loads and the magnitude of stress fields decreases. Simulation results show that the maximum principal stresses cause cracking in the layer and that the shear stresses are not high enough to cause its delamination. The thicker layer/substrate system offers a higher resistance to cracking formed at 950 °C for 6h.

Author Index

Bold page numbers indicate presenter