Advanced Characterization Techniques for Coatings and Thin Films

Room Royal Palm 4-6 - Session H1

Advanced Microstructural Characterization of Thin Films and Engineered Surfaces

Moderators: Xavier Maeder, Empa, Swiss Federal Laboratories for Materials Science and Technology, Michael Tkadletz, Montanuniversität Leoben

8:00am **H1-1 Imaging Cross-sectional Structure-property Relationship in Thin Films*, Jozef Keckes,*** Montanuniversität Leoben, Austria **INVITED**

Peculiarity of physical properties of nanocrystalline thin films resides in (i) the small crystalline size typically below 100 nm resulting in a variety of size effects, (ii) a high volume fraction of grain boundaries and (iii) a presence of gradients of microstructure and residual stresses. Those gradients may originate (i) from self-organized film growth far from the thermodynamic equilibrium, (ii) from the intentionally varying deposition conditions and/or (iii) from the inhomogeneous thermal and/or mechanical loads induced during the film service. In order to understand and optimize the functional behavior of the thin films, it is necessary (i) to analyze the properties of thin film distinct regions, like nucleation layers, interfaces and grain boundaries, and (ii) to reveal cross-sectional structure-property relationships.

In this contribution, experimental results from gradient hard and metallic thin films (e.g. TiAlN, CrN, Diamond, W, TiN/SiO_x) are discussed. The films are analyzed using a variety of novel analytical techniques developed by the group in last 5 years. Primarily, cross-sectional X-ray nanodiffraction using monochromatic point and pencil X-ray beams with a diameter or a thickness down to 30 nm was used (at ID13 of ESRF and at P03 of PETRA III) to resolve depth-resolved evolution of phases, texture, crystallite sizes and the first-order stresses across thin film cross-sections. The observed gradients are correlated with the varying film deposition conditions, providing an opportunity to optimize deposition processes. Additionally, results from strain and microstructure characterization (i) in in-situ indented TiN and (ii) in multilayered CrN-Cr thin films after wedge indentation are presented to demonstrate the correlation between the present (i) microstructure, (ii) recorded load-displacement curves as well as (iii) stress concentrations. Additionally, for a graded nanocrystalline TiAlN thin film, the comprehensive characterization of cross-sectional structure-property relationships will be used to analyze the correlation between sub-micron depth variations of fracture stresses, hardness and elastic moduli on one side, and phases, crystallite sizes, crystallographic texture, Ti/Al ratio and residual strain on the other side. Finally, the cross-sectional approach will be used to indicate the possibility of functional optimization of thin films through cross-sectional design.

8:40am **H1-3 Synchrotron and Transmission Kikuchi Diffraction Characterization of Deformed Multilayer Thin Films on Polyimide*, Mikhail Polyakov,*** *X Maeder,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; P Gruber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM-AWP), Germany*; J Michler,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Nano metallic multilayers (NMMs) are materials which consist of multiple nanometer-thick layers of different metals. NMMs are present in a variety of applications, from protective coatings to electronics to x-ray mirrors. However, the deformation mechanics of such materials, which are especially relevant for protective coatings and electronics on flexible substrates, are difficult to determine for several reasons. Firstly, the small grain sizes and layer thicknesses (<50 nm) limit the use of techniques with larger resolution limits, most notably Electron Backscatter Diffraction (EBSD). In addition, the small layer thicknesses translate to small scattering volumes for X-ray diffraction techniques, which can result in prohibitively long data collection times.

To address these specific limitations, additional characterization techniques were used. The first is Transmission Kikuchi Diffraction (TKD, also referred to as transmission-EBSD or t-EBSD). The technique is similar to EBSD in that one can map grain orientations over a large area, but it utilizes the transmitted diffraction patterns rather than the backscattered diffraction patterns. This results in an improved spatial resolution of less than 10 nm, allowing for the characterization of layers and grains with characteristic lengths below 50 nm, before and after deformation.

The second technique used was in-situ synchrotron XRD of tensile tested films. The brilliance of the synchrotron X-ray source allows for much shorter recording times than for a standard X-ray source. Therefore, a series of diffraction patterns can be collected in a reasonable amount of time during the tensile testing of thin multilayered films. Since the diffraction rings for the different materials can be distinguished, the stress for the different materials can be determined individually. In this way, the deformation of the layers can be decoupled and the contributions of the individual materials to the overall deformation behavior can be calculated.

We have demonstrated the differing load sharing contributions from varying layer thicknesses for Cu/Nb nano multilayers on polyimide [1], and the results will be compared with the deformation of Cu/Zr and Cu/CuZr multilayer samples. With Cu/Nb, Cu/Zr, and Cu/CuZr multilayers, a variety of crystal structures are present, resulting in differing deformation mechanisms.

[1] Polyakov, Mikhail N., Jochen Lohmiller, Patric A. Gruber, and Andrea M. Hodge. Advanced Engineering Materials Adv. Eng. Mater. 17.6 (2014): 810-14

9:00am **H1-4 Advanced EBSD and *in-situ* EBSD Techniques for Microstructure, Crack, Fatigue, and Plastic Deformation Characterization in Metals and Thin Films*, J Ast, Y Guo, M Polyakov, J Schwiedrzik, G Mohanty, J Michler, Xavier Maeder,*** Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The measurement of characteristics such as crystal structure, crystallographic orientation, grain dimension, and residual stress is fundamental for evaluating thin films and coatings and correlating their structures with their mechanical, chemical, or thermal properties. For such analyses in small volume materials, X-ray diffraction techniques and transmission electron microscopy are generally considered to be the tools of choice. Electron backscatter diffraction (EBSD), which can be combined with cross correlation techniques (HR-EBSD), offers the advantage of providing crystal orientation maps from which phase, grain size, grain shape, grain boundary type, texture, residual stress, and crystal defects can be determined with a resolution of 50nm. In addition, Keller and Geiss have recently demonstrated that EBSD patterns can be acquired from a thin film specimen using transmitted electrons in the SEM [1] (Transmission Kikuchi-Diffraction [TKD] or transmission-EBSD), thus improving the lateral resolution of the technique by an order of magnitude, reaching sub-10nm resolution, making it suitable for nano-crystalline materials. We applied transmission-EBSD to characterize the microstructure of PVD and electrodeposited materials. Crystallization and twinning processes have been studied for several materials, such as nanocrystalline Ni, CuNi, CuAl, and pure Cu, and the observed structures have been linked to their mechanical proprieties. We have also applied EBSD and HR-EBSD techniques together with *in-situ* micro-mechanical testing to better assess the deformation mechanisms in metals and coatings. The detailed microstructure, plastic zone size, dislocation mobility, strain, and stress can be mapped at successive deformation steps in the materials. Examples will be given for micro-cantilever bending and micro-pillar compression.

References:

[1] R.R. Keller, R.H. Geiss, *Journal of Microscopy* 2012, 245, 245–251.

9:20am **H1-5 Characterization of the Porosity of Silicon Nitride Thin Layers*, Thomas Barrès,*** *H Montigaud,* Saint-Gobain Recherche, France*; O Stephan,* Université Paris-Sud, France*; B Tribollet,* Université Pierre et Marie Curie, France*; Y Cohin,* Saint-Gobain Recherche, France*; M Boinet,* Saint-Gobain, USA

Silicon nitride (SiN_x) is commonly used as a dielectric thin film (10 to 100 nm) within stacks deposited by magnetron sputtering in the glass industry. The porosity of such thin films can be detrimental to the product durability and performances upon ageing [1].

The nanostructural characterization of silicon nitride thin films has been previously carried out by Transmission Electronic Microscopy (TEM) [2]. Thanks to several microscopy techniques such as TEM, Scanning Transmission Electronic Microscopy in High Angle Annular Dark Field mode (STEM HAADF), and Electron Energy Loss Spectroscopy (EELS), we are able to give a quantitative description of the porosity in SiN_x layers at the nanometre scale. In addition to purely topographic characteristics, EELS and HAADF measurements give access to the local composition and atomic density in the thin film. The 3D morphology of the pores was determined by observing the sample from different incidences (plane-view and cross sections obtained by means of FIB lamella).

In parallel to the microscopic approach, we estimated the porosity at a larger scale as well as the through-porosity total fraction, by using Electrochemical Impedance Spectroscopy (EIS) measurements. Impedance measurements have a high sensitivity to the pore distribution in the layer [3], providing a complementary point of view on the layer morphological characteristics to the one offered by TEM.

Finally, the evolution of the layer nanostructure is studied as a function of the SiN_x deposition parameters allowed by reactive magnetron sputtering (deposition pressure, sputtering rate, and plasma composition) as well as final characteristics (density, thickness or intrinsic stress).

References :

[1] J. Kulszyk-malecka, Diffusion studies in toughenable Low-E coatings, PHD thesis, (2012).

[2] C. Colliex, A. Gloter, M. Kociak, K. March, O. Stephan and M. Tencé, Microscopy and Analysis 26(6) (2012), 33-40.

[3] A. Perrotta, S. J. García, J. J. Michels, A-M. Andringa, M. Creatore, ACS Appl. Mater. Interfaces, (2015), 7 (29), pp 15968–15977.

9:40am **H1-6 Microsecond-Scale Chemical Reactions at Interfaces in Thermal Spray Coatings***, Anh Tran, M Hyland,* The University of Auckland, New Zealand

The possibility of extremely rapid chemical reactions at interfaces between molten metal droplets and metal substrates in thermal spray coatings is reported in this study. Nickel single molten droplet was deposited on different substrates including stainless steel, chromium and titanium at either room temperature or 300 °C by plasma spray. The splat morphology and splat-substrate interfaces were characterised using FIB and TEM. Substrate's element was found to diffuse into the nickel splat, but not vice versa. Thin layers of mixed oxides were detected at the interface of nickel droplet deposited on either chromium or stainless steel substrate, but not on titanium substrate. Instead, a relatively thick intermetallic layer with the thickness up to 1 µm composing of three different phases of $TiNi_3$, TiNi, and Ti_2Ni was found along the entire Ni-Ti interface. We also found that the chemical reactions to form interfacial layers occurred after the splat solidified, thus it is not involved in the way droplet spread on the solid surface and subsequent splat-substrate bonding.

10:00am **H1-7 Thermal Stability of Expanded Austenite formed on a DC Plasma Nitrided 316L Austenitic Stainless Steel***, André Tschiptschin, A Nishikawa, L Varela,* University of São Paulo, Brazil*; C Pinedo,* Heat Tech & University of Mogi das Cruzes, Brazil

Expanded austenite formed during low temperature plasma nitriding of austenitic stainless steels is known for its excellent wear and corrosion resistance especially when working in systems where galling, erosion-corrosion, cavitation-erosion and pitting corrosion resistance are a major concern. These wear and corrosion properties may degrade by exposure of the surface hardened steel to high temperatures, between 400 °C and 700 °C. In the present work, DC low temperature plasma nitrided 316L austenitic stainless steel (400 °C for 20 hours) was heated up to investigate the stability of the expanded austenite layer in the range 400 °C < T < 700 °C. Time-resolved X-ray diffraction experiments were undertaken in a thermomechanical simulator coupled to the Brazilian National Synchrotron Light Source. Two series of experiments were carried out: a) isothermal treatments conducted at temperatures between 400 and 600 °C for 4h and b) a continuous heating experiments from room temperature up to 700 °C, with a heating rate varying from of 6 °C/min to 60 °C/min. Results show that during the isothermal heat treatments, expanded austenite remains approximately stable up to 400 °C, without losing nitrogen and maintaining its lattice parameter. For isothermal holding temperatures higher than 450 °C a continuous decrease in expanded austenite in the time span of the experiments is observed, presumably due to diffusion of nitrogen to the matrix. This phenomenon is followed by formation of ferrite and chromium nitrides precipitation. In the continuous heating experiments expanded austenite decomposition into three products is observed: ferrite, austenite, and nitrides. As expected from thermal an activated reaction, the critical temperature of this transformation is dependent on the heating rate. At the heating rate of 12 °C/s the initial 0.385 nm expanded austenite lattice parameter increased up to 0.3875 nm at 425 °C due to thermal expansion, indicating an average thermal expansion, over the analyzed expanded austenite layer, of 5×10^{-5} K^{-1}. This value is much lesser than the values reported for the thermal expansion coefficients of the fcc austenitic phase in austenitic stainless steel $K = 15 \times 10^{-5}$ K^{-1}, indicating that expanded austenite is also losing compressive residual stresses during heating.

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