Advanced Characterization, Modelling and Data Science for Coatings and Thin Films
Room Palm 3-4 - Session CM1-2-TuA

Spatially-resolved and In-Situ Characterization of Thin Films and Engineered Surfaces II

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Michael Tkadletz**, Montanuniversität Leoben, Austria

1:40pm **CM1-2-TuA-1 Structural Evolution of Nanoparticles Under Realistic ConditionsObserved with Bragg Coherent X-Ray Imaging*, Marie-Ingrid Richard (marie-ingrid.richard@cea.fr),*** CEA Grenoble, France **INVITED**

The advent of the new 4th generation x-ray light sources represents an unprecedented opportunity to conduct *in situ* and *operando* studies on the structure of nanoparticles in reactive liquid or gas environments. In this talk, I will illustrate how Bragg coherent x-ray imaging [1] allows to image in three dimensions (3D) and at the nanoscale the strain and defect dynamics inside nanoparticles as well as their refaceting during catalytic reactions [2–4]. As an example, we successfully mapped the lattice displacement and strain of a Pt nanoparticle in electrochemical environment (see Figure 1). Our results reveal that the strain is heterogeneously distributed between highly- and weakly-coordinated surface atoms, and propagates from the surface to the bulk of the Pt nanoparticle as (bi)sulphates anions adsorb on the surface [5].

We will also discuss the possibility to measure particles as small as 20 nm [6] and to enable high-resolution and high-energy imaging with Bragg coherent x-ray diffraction at 4th generation x-ray light sources [7]. Finally, I will highlight the potential of machine learning to predict characteristic structural features in nanocrystals just from their 3D Bragg coherent diffraction patterns [7].

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[3] J. Carnis et al., *Twin Boundary Migration in an Individual Platinum Nanocrystal during Catalytic CO Oxidation*, Nat. Commun. **12**, 5385 (2021).

[4] M. Dupraz et al., *Imaging the Facet Surface Strain State of Supported Multi-Faceted Pt Nanoparticles during Reaction*, Nat. Commun. **13**, 1 (2022).

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[6] M.-I. Richard et al., *Bragg Coherent Diffraction Imaging of Single 20 Nm Pt Particles at the ID01-EBS Beamline of ESRF*, J. Appl. Crystallogr. **55**, 621 (2022).

[7] M.-I. Richard et al., *Taking Bragg Coherent Diffraction Imaging to Higher Energies at Fourth Generation Synchrotrons: Nanoscale Characterization*, ACS Appl. Nano Mater. **6**, 10246 (2023).

[8] B. Lim et al., *A Convolutional Neural Network for Defect Classification in Bragg Coherent X-Ray Diffraction*, Npj Comput. Mater. **7**, 1 (2021).

2:20pm **CM1-2-TuA-3 Grain Boundary Segregation/Complexions in MT-CVD Ti(C,N) Thin Hard Coatings Analyzed by Nano-SIMS and Atom Probe Tomography*, Idriss El Azhari (idriss.elazhari@uni-saarland.de),*** *J. Barrirero,* Saarland University, Germany*; N. Valle,* Luxembourg Institute of Science and Technology (LIST), Luxembourg*; J. García,* Sandvik Coromant, Sweden*; C. Pauly, F. Soldera,* Saarland University, Germany*; L. Llanes,* Universitat Politècnica de Catalunya, Spain*; F. Mücklich,* Saarland University, Germany

Ti(C,N) is one of the most utilized thin hard coatings in metal-cutting industry in the last twenty years. In prior works, the authors carried out multi-scale testing and characterization experiments in which industrial cutting inserts coated with Ti(C,N) wear resistant hard coatings are contrasted to Zr(C,N) coated counterparts. The purpose was to comprehend the influence of the coating's microstructural features **on the deformation behavior of each coating and the corresponding impact on the entire coated cutting tool system**. The investigation showcased that the more compatible coefficient of thermal expansion of Zr(C,N) with the substrate, the better cohesive strength at the grain boundaries and the plastic deformation were found to assign to the Zr(C,N) coated hardmetal improved structural integrity and fracture toughness in comparison to Ti(C,N) [1,2].

In this work, the focus is shifted toward Ti(C,N) to understand the correlation between deposition temperature and its impact on the microstructural features and segregation/complexions at the grain boundaries. For this purpose Ti(C,N) was deposited on a WC-Co substrate at two different temperatures (885°C and 930°C) using a moderate temperature CVD process (MT-CVD). Electron Backscatter Diffraction (EBSD) is used to examine microstructures. High-resolution secondary ion mass spectrometry imaging (nano-SIMS) and atom probe tomography (APT) were combined to investigate compositional variations inside single crystals and segregation at the grain boundaries. It is shown that segregation of chlorine at the grain boundaries is affecting not only the grain size of the columnar crystals, but texture and crystal shapes are indeed affected and modified as the chlorine concentration is decreasing with increasing temperature deposition. Methods to tailor the microstructure of these compounds are discussed and suggested.

Bilbliography

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[2]I. El Azhari, J. Barrirero, N. Valle, J. García, L. von Fieandt, M. Engstler, F. Soldera, L. Llanes, F. Mücklich, Impact of temperature on chlorine contamination and segregation for Ti(C,N) CVD thin hard coating studied by nano-SIMS and atom probe tomography, Scripta Materialia. 208 (2022) 114321. https://doi.org/10.1016/j.scriptamat.2021.114321.

4:00pm **CM1-2-TuA-8 *In situ* Studies of Nucleation and Growth by High Energy X-Ray Scattering*, Jens Birch (jens.birch@liu.se),*** *N. Ghafoor, F. Eriksson,* Linköping University, Sweden*; S. Stendahl,* Uppsala University, Sweden*; S. Dorri, S. Nayak,* Linköping University, Sweden*; L. Rogström,* Uppsala University, Sweden **INVITED**

The understanding of the formation of nanoscale structures and their properties, requires time-resolved analytical tools able to probe into the nano realm. High energy (HE) X-rays, with wavelengths in the 0.01-10 nm range, provided by state-of-the-art synchrotrons feature four synergetic properties: High penetration depth, small scattering angles, very low beam divergence, and high intensity. This makes it easy to design in situ sample environments for experiments providing a large amount data using a sub-µm probe size, at a high rate data acquisition. Thus, HE X-rays lend themselves well for *in situ* and *operando* time-resolved experiments to shed light onto elusive nanoscale phenomena. A purposefully designed UHV-based deposition system for time-resolved *in situ* studies of thin film nucleation and growth processes is presented with examples ranging from high precision nm-period multilayer neutron mirrors to wear-resistant coatings, grown by magnetron sputtering and cathodic arc deposition at the High Energy Materials Science beamline P07 at PETRA III in Hamburg.

In situ time-resolved HE XRD,was used to study microstructural evolution of Ni/Ti:B_4C multilayer neutron mirrors in real time. Combining incorporation of $^{11}B_4C$ with temporally modulated ion-assistance during deposition, it was possible to achieve amorphous layers with interface widths s=4 Å (a reduction from 7 Å for state-of-the-art). The neutron reflectivity was observed to increase by 43%, implying up to 10x higher neutron throughput and a significantly increased neutron wavelength range for future neutron guides.

Another example is *in situ* characterization of epilayer strain evolution during magnetron sputter epitaxy of single crystal 6 nm-bilayer periodic superlattices of$CrB_{1.7}/TiB_{3.3}(0001)/Al_2O_3(0001)$. XRD revealed a rapid initial relaxation of superlattice-substrate misfit strain, from -0.067%, in the first bilayer period to -0.0013 % during growth of the 2nd bilayer. This observation precludes substrate misfit strain as driving force for an observed B segregation to tissue phases extending transversely through several bilayer periods.

Phase stability during cathodic arc as well as magnetron syntheses of polycrystalline TiAlN tool coatings were studied. The precipitation sequence and size evolutions of metastable cubic Ti-rich TiAlN nanocrystallites (responsible for hardening) and Al-rich wurtzite phase (causing over-hardening) could be followed in detail.

The improved prospects for future availability of the *in situ* deposition system upon installation of a large 1500 kg capability hexapod at the Swedish Materials Science beamline P21 will be presented.

4:40pm **CM1-2-TuA-10 Multidimensional Elemental and Molecular Analysis for Surface & Interface Studies***, **Kayvon Savadkouei (kayvon.savadkouei@horiba.com)***, HORIBA, USA*; P. Chapon, A. Stankova,* HORIBA, France

Surface and Interface corrosion studies require the use of complementary analytical techniques as each instrumentation provides results based on the interaction of the investigated material with a probing medium [1].

Obtaining elemental and molecular information for different probing size and depth are especially crucial.

HORIBA offers a Platform with multiple instruments able to tackle these complex analytical challenges.

Glow Discharge relies on plasma to sputter a representative area of a material and provides fast elemental depth profile with nanometer resolution [2].

Coupling GD and Raman microscopy allows us to obtain molecular information at various depths with micrometer lateral resolution [3,4].

Applying the GD software ideal to follow transient signals to a simultaneous ICP instrument coupled with an electrochemical cell (AESEC technique) offers deep insight on dissolution mechanisms and metallic surfaces performances [5].

We will illustrate the benefit of this Surface Platform for Elemental and Molecular Analysis with selected results on metallic parts for high temperature fuel cells, hard facing materials in Na fast reactors, perovskite solar cells, hydratation of anodic films and DCL coatings on bipolar plates.

References:

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