Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
Room On Demand - Session HP

Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes (Symposium H) Poster Session

HP-1 Expanding the Information and Increasing the Reliability of XPS Analysis, ***Donald Baer (don.baer@pnnl.gov)***, Pacific Northwest National Laboratory, USA; *K. Artyushkova,* Physical Electronics, USA; *C. Easton,* CSIRO, Australia; *M. Engelhard,* Pacific Northwest National Laboratory, USA; *A. Shard,* National Physical Laboratory, UK

Because of the importance of surfaces, interfaces, and thin films in many areas of science and technology, use of X-ray Photoelectron Spectroscopy (XPS) has grown exponentially for the past two decades. One impact of this rapid increase is that many analysts have limited experience or detailed knowledge of the method. This has led to two interrelated issues. First there is an increase of inaccurate or incorrect analyses of XPS data reported in journal publications. An examination of six months of XPS data in three quality journals indicated that 30% of the reported analyses had significant misleading errors and another 30% had the potential to significantly impact the conclusions. The error rate was even greater for papers reporting fitting of spectra. The second challenge is that much of the data analysis is conducted in the most simplistic manner and does not take full advantage of the information that XPS can provide regarding layered structures, including thickness determination and uniformity. Multiple efforts are needed, some underway, to address these two challenges. Raising community awareness of the issues and opportunities is a critical first step. The error rate assessment also identified the types of errors occurring, providing analysts with information of common problems. A survey of AVS members indicated that guides, tutorials, protocols, and standards could help the community. To that end, a collection of XPS guides and introductions to various aspects of XPS has been prepared and published in Journal of Vacuum Science and Technology A. These papers address a range of topics required for quality XPS including preparation and planning, instrument setup and data collection, quantitative data analysis and curve fitting and depth information. These papers both provide guidance for minimizing errors and suggest the full range of information that might be extracted. Guides aimed at the use of XPS for specific systems such as polymers, catalysts, nanoparticles, and epitaxial films provide application specific guidance extending beyond the most common analysis approaches. Increasingly XPS analyses may involve modeling of signals expected from complex surface structures, including ultrathin films, epitaxial layers, and nanoparticles using programs such as SESSA, Multiquant and QUASES. Other pathways to advancing XPS include using high energy X-rays (HAXPES), an expanding range of environmental conditions (NAP-XPS), reporting data according to the FAIR data principles, the development of expert systems that codify and apply the hundreds of years of XPS experience, and the application of AI for enhancing data analysis and recognizing faulty data.

HP-2 Electric Field Strength-Dependent Accuracy of TiAlN Thin Film Composition Measurements by Laser-Assisted Atom Probe Tomography, ***Marcus Hans (hans@mch.rwth-aachen.de)***, *J. Schneider,* RWTH Aachen University, Germany

Accurate quantification of absolute concentrations represents a major challenge for atom probe tomography (APT) since the field evaporation process is affected significantly by the measurement parameters. In the present work we investigate systematically the effect of laser pulse parameters on the accuracy of laser-assisted APT for a TiAlN thin film previously quantified by ion beam analysis, combining Rutherford backscattering spectrometry and time-of-flight elastic recoil detection analysis. The electric field strength is estimated from the Al^{2+}/Al^{+} charge state ratio for all systematically varied measurement parameters. Subsequently, the absolute concentrations from laser-assisted APT are compared to ion beam analysis data. An increase of the electric field strength from approximately 25 to 28 V nm^{-1} improves the accuracy of absolute concentrations measured by laser-assisted APT from 11.4 to 4.1 at.% for N, from 8.8 to 3.0 at.% for Al and from 2.8 to 0.9 at.% for Ti. Our data emphasize that the measurement accuracy of laser-assisted APT for TiAlN is governed by the electric field strength. It is shown that the smallest compositional discrepancies between ion beam analysis and APT are obtained for the maximum electric field strength of approximately 28 V nm^{-1} at 10 pJ laser pulse energy. This can be rationalized by considering the enhanced ionization of neutral fragments caused by the increased electric field strength.

HP-3 Integrated Atom Probe/tEBSD for Grain and Phase Boundary Analysis of Coatings and Thin Films, ***Robert Ulfig (robert.ulfig@ametek.com)***, *Y. Chen, K. Rice, T. Prosa,* CAMECA Instruments Inc., USA

Transmission EBSD mapping offers the ability to target site-specific grain or phase boundaries for Atom Probe Tomography (APT) analysis, and correlate boundary chemistries with grain misorientations. In this study we demonstrate that high-resolution transmission electron back scattering diffraction (tEBSD) maps can be acquired on needle-shaped APT specimens that consist of grains of size ranging from few hundred nanometers to few micrometers. The use of this correlative technique will be demonstrated with thermal barrier coatings (TBCs) used in turbine engines to operate at temperatures greater than the melting temperatures of engine components and consequently achieve better propulsive power performance and fuel efficiency. The general structure consists of three layers: a top is a coat made of yttrium-stabilized ZrO_2 (or YSZ), which has excellent thermal resistivity, a thermally grown oxide (TGO) scale, that consists of a-alumina grains, and a bond coat layer at the coating/substrate interface that improves adhesion of the ceramic layers on the superalloy substrate.

HP-4 Sub-50 nm X-ray Diffraction Reveals Nanoscale Residual Stress and Microstructure Distributions across the Cutting Edge Area of a TiN Coating on WC-Co, ***Michael Meindlhumer (Michael.Meindlhumer@oeaw.ac.at)***, *N. Jäger, S. Spor,* Montanuniversität Leoben, Austria; *M. Rosenthal,* ESRF Grenoble, France; *H. Hruby,* eifeler-Vacotec GmbH, Düsseldorf, Germany; *J. Keckes, C. Mitterer,* Montanuniversität Leoben, Leoben, Austria; *R. Daniel, J. Keckes, J. Todt,* Montanuniversität Leoben, Austria

The nanoscale microstructural and residual stress gradients across hard coatings on cutting tools are of high scientific and industrial interest. Here, cross-sectional X-ray nanodiffraction with a beam size of 35×25 nm² was used to retrieve structural and mechanical gradients in the cutting edge area of a ~2 µm thick TiN coating deposited by cathodic arc evaporation on a WC-Co substrate. Scanning small-angle X-ray scattering microscopy (SAXSM) is presented and utilized for the first time to investigate the nanoscale defect density in the cutting edge area. At the cutting edge, interface-like planar domains of high scattered intensity were indicated, while a gradual increase of the SAXS intensity at the rake face was correlated with pores found by scanning electron microscopy. Furthermore, the coating's <111> fibre texture axis orientation correlates with the substrate's surface normal, showing abrupt orientation changes across the former mentioned interface-like structures. The planar regions next to the edge exhibit gradual and constant stress profiles with anisotropic defect build-ups on the flank and rake faces, respectively. Directly at the edge, nonlinear lateral and cross-sectional compressive residual stress gradients ranging from ~0 to −3 GPa were observed, which together with the interface-like planar domains may represent a reliability issue during operation.

HP-5 e-Poster Presentation: Nanoindentation Analysis as a Two-Dimensional Tool for Mapping the Mechanical Properties of Complex Microstructures, ***Nicholas Randall (nicholas.randall@alemnis.ch)***, *J. Breguet,* Alemnis, Switzerland

Instrumented indentation (referred to as nanoindentation at low loads and low depths) has now become established for the single point characterization of hardness and elastic modulus of both bulk and coated materials. This makes it a very good technique for measuring mechanical properties of homogeneous materials. However, many composite materials comprise material phases that cannot be examined in bulk form ex-situ (e.g., carbides in a ferrous matrix, calcium silicate hydrates in cements, etc.). The requirement for in-situ analysis and characterization of chemically complex phases obviates conventional mechanical testing of large specimens representative of these material components. This paper will focus on new developments in the way that nanoindentation can be used as a two-dimensional mapping tool for examining the properties of constituent phases independently of each other. This approach relies on large arrays of nanoindentations (known as grid indentation) and statistical analysis of the resulting data.

HP-6 Microstructural Influences on the Fracture Properties of CrN Coatings*, Rainer Hahn (rainer.hahn@tuwien.ac.at)*, *S. Rosenecker,* CDL-SEC, TU Wien, Austria*; T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* TU Wien, CDL-SEC, Austria

Transition Metal Nitrides (TMN) are well known for their good mechanical stability, chemical inertness, as well as tribological properties. Hence, they successfully found application in the metal forming industry, and are in use as protective coatings in the automotive and aerospace industry. Besides TiN, CrN is one of the most used and best investigated hard coatings, preferably applied in conditions that require a low coefficient of friction. A decisive disadvantage of these hard coatings, however, is their low fracture tolerance. Premature failure of the coating due to crack initiation and propagation leads to economic disadvantages or completely excludes an application. In recent years, micromechanical testing methods have made it possible to measure and specifically improve precisely fracture toughness of thin film materials. There are various methods known for measuring K_{IC} obtaining all advantages and drawbacks, especially with respect to intrinsic material characteristics and accuracy.

In this contribution, we perform distinct micromechanical tests on cathodic arc evaporated CrN coatings. These coatings were deposited with different bias voltages and deposition temperatures in order to obtain a variation in both, microstructure (specifically crystallite size) and defect density. The importance of the microstructure on fracture characteristics has recently shown by Ast et al. for Ti-Al-N deposited by diverse PVD techniques [1]. However, a clear correlation between the column size and the density of column boundaries is still missing.

We found a significant influence of the residual stress state on the fracture properties of such hard coatings using the indentation fracture method. Furthermore, we used pillar splitting and cantilever bending tests to determine the intrinsic fracture toughness of our coatings with respect to the microstructure and defect density. These results were complemented by HR-TEM investigations together with x-ray diffraction studies, and nanoindentation tests.

References

[1] Ast J., et al., (2019). Fracture toughness determination of arc-PVD and HiPIMS hard coatings by micro-cantilever and pillar splitting tests.

HP-9 Thin Film Characterization Utilizing Broad Ion Beam Specimen Preparation and FESEM*, Natasha Erdman (erdman@jeol.com)*, *N. Inoue,* JEOL USA Inc, USA

Examination of materials cross sections often provides essential information about the crystal structure, layer or film thicknesses, existence of voids or cracks and other properties that might impact materials performance and reliability. Cross-sectional observation is especially essential in thin film technology, to examine layer thickness, deposition integrity (voids/adhesion), as well as film growth and crystallographic orientation. Currently various methods are used to prepare specimen cross sections for scanning electron microscope (SEM) observation. Mechanical methods of cutting and polishing are widely used, particularly for metallographic sample preparation. However, mechanical polishing presents several problems: a) in composite materials with different hardness values, the polished surface becomes uneven as the softer components are cut faster and more easily than the harder components; b) in soft materials, particles of hard abrasive can be buried in the material being polished; c) in materials with voids, the edges of the voids can stretch and deform; e) for metals, due to the strain caused by mechanical polishing on the polished surface, the information about the crystal structure by means of electron back-scatter diffraction (EBSD) becomes difficult or impossible to obtain; f) fine features like hairline cracks and small voids can get smeared shut and will not be recognized as such.

This paper presents utilization of broad ion beam instrument (JEOL CP polisher) for cross-sectional preparation of various thin film/substrate combinations. This table top instrument utilizes Ar ion beam to produce large area cross-sections of materials, with the ability to employ cryogenic (LN2) temperatures to address beam sensitive and eutectic metal systems. Moreover, the use of FE-SEM equipped with in-lens detectors and high sensitivity backscatter detecotr allows observation of the resulting samples to investigate nanoscale features, including voids, grain boundaries and layers. Additionally, EDS and EBSD can be utilized to provide additional characterization of the thin film specimens in terms of compositional variations and crystallographic orientation.

We will present examples of Zn thin films - depending on the film composition these may require cryogenic preparation to preserve film integrity. Additionally we would present examples of other materials - anodized films, evaporated metal thin films, solar films, etc.

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