## Advanced Surface Engineering
## Room: 22 - Session SE+NS-MoM

### Nanostructured Thin Films and Coatings I: Interface Aspects
### Moderator: J. Patscheider, EMPA, Switzerland

8:40am **SE+NS-MoM2 Ion-guided Phase Separation of Carbon-Nickel Composite Films during Ion Beam Assisted Deposition: 3D Sculpting at the Nanoscale**, ***G. Abrasonis,*** Helmholtz-Zentrum Dresden-Rossendorf, Germany, *M. Krause,* Helmholtz-Zentrum Dresden-Rossendorf and Technische Universität Dresden, Germany, *T.W.H. Oates,* Leibniz-Institut für Analytische Wissenschaft, Germany, *A. Mücklich, S. Facsko,* Helmholtz-Zentrum Dresden-Rossendorf, Germany, *C. Baehtz, A. Shalimov,* Helmholtz-Zentrum Dresden-Rossendorf, Germany and European Synchrotron Radiation Facility, France, *S. Gemming*, Helmholtz-Zentrum Dresden-Rossendorf, Germany

Ion assistance during film growth provides unique opportunities to influence the microstructure due to energy transfer and imposed directionality. During nanocomposite film growth at low temperatures, phase separation occurs at the growing film surface. Ion-assistance is a key parameter to control the surface processes during multiphase film growth, and hence the resulting nanocomposite morphology. A systematic study of ion irradiation as a pure energy and momentum transfer agent in the context of surface diffusion assisted phase separations is, however, lacking. Here the influence of low energy (50-130 eV) assisting $Ar^+$ ion irradiation on the morphology of C-Ni thin films will be reported. Ion-beam assisted deposition (IBAD) promotes the columnar growth of carbon encapsulated metallic nano-columns at low deposition temperatures for $Ar^+$ ion energy ranges of 50-100 eV. Moreover, the momentum transfer results in a tilting of the columns relative to the film surface. The potential to grow complex matrix encapsulated metallic structures such as chevrons is demonstrated. Furthermore, a window of deposition conditions will be reported where the ion assistance leads to the formation of regular 3D nanopatterns with well-defined periodicity. The influence of such anisotropic film morphology on the optical properties is highlighted.

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9:00am **SE+NS-MoM3 Interface Phenomena in Nanostructured Thin Films and Coatings**, ***D. Rafaja***, Freiberg University of Technology, Germany **INVITED**

The properties of nanostructured thin films and coatings are strongly influenced by the structure of internal interfaces. Thus, the understanding of the formation of the interfaces and the knowledge of the relationship between the microstructure and the materials properties are the first steps in designing nanostructured materials with tailored properties. This talk will focus on partially coherent interfaces between adjacent crystalline phases in nanostructured thin films and coatings, discussing the mechanisms of their formation, showing the capabilities of experimental methods for microstructure analysis to detect these interfaces and to describe their structure on the atomic scale, and recognizing the influence of the interfaces on the materials properties.

The interface phenomena and their impact on hardness and thermal stability of nanostructured thin films and coatings will be illustrated on physical vapor deposited transition metal nitrides containing aluminum and/or silicon, where the internal interfaces form as a consequence of the decomposition of metastable supersaturated solid solutions. It will be shown how the local fluctuations of the chemical composition arising during the deposition process and the local strain fields resulting from differences in the interatomic distances at partially coherent interfaces influence the decomposition process and the stability of the metastable phases.

The description and quantification of the interface phenomena on atomic scale would be impossible without a detailed microstructure analysis that is required to reveal the constitution of the nanostructured materials, to reproduce the structure of the internal interfaces and to assess the coherence of the interfaces. Hence, this talk will also recapitulate the recent developments in the microstructure analytics on the nanostructured thin films and coatings.

9:40am **SE+NS-MoM5 Mechanical Properties, Fracture Toughness, and Thermal Stability of CrN/AlN Superlattice and Multilayer Thin Films**, *M. Schlögl, B. Mayer, J. Paulitsch, J. Keckes, C. Kirchlechner,* ***P.H. Mayrhofer***, Montanuniversität Leoben, Austria

Transition metal nitrides, such as CrN are highly attractive materials for a wide range of applications due to their outstanding properties like high hardness, excellent corrosion and oxidation resistance. Consequently, many research activities deal with their synthesis-structure-properties-relations. However, it has been reported that CrN/AlN superlattice coatings improve the mechanical properties compared to single CrN especially when keeping the AlN in its metastable cubic phase. Hence, we investigated the influence of the layer thickness of CrN on the stabilization of c-AlN and the critical layer thickness for AlN before transforming into the stable wurtzite phase. Furthermore, stress measurements and thermal stability were accomplished by the in-situ wafer curvature method during vacuum annealing to 700°C, differential scanning calorimetry to 1500°C and hardness measurements after annealing up to 1100°C.

The fracture toughness of the coatings is studied by means of in-situ scanning electron microscopy and transmission electron microscopy microbending and microcompression tests. The small test-specimens are prepared by focused ion beam milling of individual free-standing thin films. As generally monolithic coatings with their columnar structure provide low resistance against crack formation and propagation we perform our studies for CrN films, CrN/AlN multilayers and the CrN/AlN superlattice as mentioned above. Especially the multilayers and superlattices provide additional interfaces perpendicular to the major crack-propagation-direction. Adjusting the AlN layer-thicknesses to allow for cubic or wurtzite structure enables to study the influence of the extremely stress sensitive cubic-to-wurtzite AlN phase transformation on the crack propagation.

The microtests clearly demonstrate that the monolithic CrN as well as the CrN/AlN multilayer coating with the wurtzite AlN layers crack with the behavior and features for brittle fracture. Contrary, the CrN/AlN multilayer coatings composed of cubic stabilized AlN layers are able to provide resistance against fatal crack propagation. Hence, they allow for significantly higher loads during the microbending and microcompression tests. Detailed structural investigations, in-situ and after the tests, suggest that the cubic AlN layers, which are stabilized by coherency strains in the CrN/AlN multilayer coatings, phase transform with the connected nature expansion when experiencing additional strain fields and thereby hinder crack propagation.

10:00am **SE+NS-MoM6 High-temperature Nanoindentation of Hard Coatings**, ***M. Rebelo de Figueiredo***, University of California Berkeley, *M. Tkadletz,* Materials Center Leoben, Austria, *M. Schlögl, R. Hollerweger, P.H. Mayrhofer, C. Mitterer,* Montanuniversität Leoben, Austria, *P. Hosemann*, University of California Berkeley

In the past decades, measurement techniques to probe the mechanical properties of hard coatings have been evolved dramatically and nowadays a wide variety of methods and devices are available. Within the field of evaluating the hardness of coating materials, nanoindentation has been established as a standard method utilizing the Oliver and Pharr approach. The measurements are commonly performed at room temperature. Industrial applications like metal cutting, however, demand resistance to wear also at temperature levels of up to 1000°C, which can easily be reached in the contact zone between a coated tool and the machined part. Therefore, knowledge about the mechanical properties of hard coatings at elevated temperatures is of vital importance. Nanoindentation devices allowing to go to temperatures as high as 750°C became available in recent years. While it appears simple to install heating devices in a nanoindenter, the minimization of the thermal drift, tip durability, and environmental control are a particular challenge to perform measurements at these temperatures. Therefore, significant efforts in monitoring all effects of a measurement performed at these conditions need to be spent in order to gain valid indentation data.

Within the present work, a series of different hard coatings were analyzed, utilizing nanoindentation experiments up to 750°C. The coatings evaluated cover selected samples representing the state-of-the-art employed in cutting operations like $Al_2O_3$ and TiAlN as well as newly developed coating materials like TiAlTaN. Possibilities and experimental limitations of high-temperature nanoindentation are critically discussed. A sound knowledge of the dependence of hardness on microstructural changes occurring at elevated temperatures provides the basis for the further development of coating materials and design.

10:40am **SE+NS-MoM8 Improving the Phase Stability of Metastable Aluminum Oxide Thin Films**, *F. Nahif, H. Bolvardi, D. Music, S. Mráz,* ***J.M. Schneider***, RWTH Aachen University, Germany

Charge state resolved ion energy distribution functions (IEDFs) of $Al^+$, $Al^{2+}$ and $Al^{3+}$ were measured as a function of Ar

pressure in the range from $5.7 \times 10^{-5}$ to 2.13 Pa (0.01 to 256 Pa cm). A close to monoenergetic beam of $Al^+$ ions was obtained in an Ar/O2 mixture at 128 Pa cm. $Al_2O_3$ films are deposited employing this monoenergetic $Al^+$ beam using a substrate bias potential to increase the ion energy. A critical $Al^+$ ion energy of 40 eV for the formation of the α-$Al_2O_3$ phase at a substrate temperature of 720 °C is determined. This energy is used as input for classical molecular dynamics and Monte-Carlo based simulations of the growth process, as well as *ab initio* calculations. The combination of theory and experiment indicates that in addition to the well known surface diffusion the previously non considered diffusion in sub-surface regions is an important atomistic mechanism in the phase formation of $Al_2O_3$. Using density functional theory and cathodic arc deposition experiments the effect of Si and Y addition on the stability of γ- and α-$Al_2O_3$ has been investigated. Si additives clearly shift the relative stability towards the γ-phase which can be understood based on the electronic structure. As the additive concentration increases, strong silicon-oxygen bonds are formed giving rise to the observed stabilization of the γ-phase.

11:00am **SE+NS-MoM9 Thermal Stability of $(Al_xCr_{1-x})_2O_3$ Solid Solution Coatings Grown by Cathodic Arc Evaporation**, *V. Edlmayr, M. Pohler,* University of Leoben, Austria, *I. Letofsky-Papst,* Graz University of Technology, Austria, ***C. Mitterer***, University of Leoben, Austria

Corundum-type $(Al_xCr_{1-x})_2O_3$ coatings were grown by reactive cathodic arc evaporation in an oxygen atmosphere using AlCr targets with an Al/Cr atomic ratio of 1. Since the $(Al_xCr_{1-x})_2O_3$ solid solution shows a miscibility gap below 1300°C, where spinodal decomposition is predicted, the microstructural changes upon annealing were investigated by a combination of transmission electron microscopy, X-ray diffraction, Raman spectroscopy and differential scanning calorimetry. The as-deposited coating consists primarily of the corundum-type $(Al_xCr_{1-x})_2O_3$ solid solution, with smaller fractions of cubic $(Al_xCr_{1-x})_2O_3$. An additional Al-rich amorphous phase and a Cr-rich crystalline phase stem from the droplets incorporated. The corundum-type $(Al_xCr_{1-x})_2O_3$ was still present after vacuum annealing at 1050°C for 2 hours, whereas additional α-$Al_2O_3$ and $Cr_2O_3$ phases were formed due to decomposition of the cubic $(Al_xCr_{1-x})_2O_3$ phase. Likewise, Cr and $Cr_2O_3$ have been detected in the annealed coating, most probably originating from the partial oxidation of Cr-rich droplets. Upon crystallization of the amorphous phase fractions present, γ-$Al_2O_3$ is formed, which partially transforms in α-$Al_2O_3$. No evidence for decomposition of the corundum-type $(Al_xCr_{1-x})_2O_3$ solid solution could be found within the temperature range up to 1400°C.

11:20am **SE+NS-MoM10 Protective Coatings Against Corrosion and Wear for 3D Components with Combined ALD and PVD Techniques**, ***S. Ek***, Picosun, Finland

Corrosion-related problems have always been a major challenge in various industries because of the components' shortened lifetime. Huge efforts are being made to improve the current corrosion protection procedures and to develop new corrosion preventing techniques. The objective is to find more efficient, environmentally sustainable, and cost-effective solutions for advanced corrosion protection of materials. However, in some applications it is not only corrosion protection that is needed but also wear resistance is required.

Relatively thick PVD coatings are generally used in applications where wear resistance is required. However, achieving simultaneous corrosion protection with that kind of coatings is challenging because the coating doesn't grow conformally and uniformly enough on the nano/microscale details of the surface of the protected material. This is where ALD coatings are needed: they enable reliable, long-term corrosion resistance through dense, uniform and conformal layers and they block the possible cracks, pinholes and nano/microscale voids and irregularities of the PVD layer, thus improving and securing the performance of the PVD coatings. At the same time, ALD contributes to structural strengthening and better chemical stability.

The choice and composition of the ALD coatings for corrosion protection depend on the substrate material and the kind of environmental conditions to which the protected components are exposed. Especially, certain metal oxides or their laminates or mixtures deposited by ALD form efficient and functional corrosion protection layers. Optimization of the protective thin film thickness and composition has been performed during the last three years in the European Union 7$^{th}$ Framework Program collaborative project CORRAL ("Corrosion protection with perfect atomic layers" [CPFP213996-1]).

In the present work, high-quality coatings with less than 0.001 % porosity were achieved. The coatings were able to seal 100Cr6 steel substrates for over 800 h in neutral salt spray tests (NSS). The lifetime of 3D test components was increased by a factor of 3-10 depending on the substrate material.

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