## Advanced Characterization Techniques for Coatings, Thin Films, and Small Volumes
## Room Golden State Ballroom - Session HP-ThP

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

**HP-ThP-1 e-Poster Presentation: Strategies for Increasing the Fracture Toughness of Hard Coatings Using CrN as a Role Model***, **Rainer Hahn (rainer.hahn@tuwien.ac.at)**, S. Rosenecker, D. Forstner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, 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, aerospace, and energy industry. Besides TiN, CrN is one of the most applied and investigated hard coatings. 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 for safety reasons.In recent years, micromechanical testing methods have made it possible to measure and specifically improve the fracture toughness of thin film materials [1]. This study focuses on microcantilever bending tests [2].

In this contribution we present three possible strategies for enhancing the fracture toughness of cathodic arc evaporated CrN coatings: toughening by grain refinement, multilayer toughening, and alloying approaches. While our first approach—grain refinement—did not lead to a significant toughness increase, we could observe an increase in fracture toughness and hardness for the other two strategies. Hereby, superlattice (multilayered) systems, CrN/TiN in our case, show the highest potential with an increase from 2.0 MPa·m$^{1/2}$ and 20 GPa for pure CrN up to 3.7 MPa·m$^{1/2}$ and 30 GPa respectively. Nonetheless, the alloying of Si (the maximum Si content was 10 at.%) to CrN as the second promising approach still yields an increase in toughness up to ~3.0 MPa·m$^{1/2}$ and 28 GPa. Besides the mechanical characterization of our samples, we also performed extensive X-ray diffraction studies and high-resolution TEM studies to describe the structure and morphology.

Keywords: Hard Coatings, Physical Vapor Deposition, Micromechanical Testing, Fracture Toughness

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**HP-ThP-2 Insights on Fracture and Fatigue Mechanisms of Hard Protective Coatings***, **Lukas Zauner (lukas.zauner@tuwien.ac.at)**, R. Hahn,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; H. Riedl,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Tailoring the intrinsic fracture characteristics of hard protective coatings towards the fatigue properties of state-of-the-art bulk materials is paramount for the application of innovative coating materials extending the fatigue-life of high-performance components. Thus, an in-depth knowledge on the failure pathways of ceramic-based thin films – generally associated with lack in intrinsic ductility – but also coated components under long-term mechanical and/or thermal loading is essential to extend their lifetime. In consequence, understanding and implementing coating concepts that allow for a controlled, and hence predictable crack propagation throughout their operating spectrum are of major interest for various industrial applications. Despite recent advances [1], literature reports on the fatigue resistance of especially hard ceramic coatings, but also coated components in general, are relatively rare with a strong approach via macroscopic test facilities. Within this study we present a methodical approach to understand the failure behaviour on different length scales utilizing model systems (*i.e.*, Cr and Cr-based compounds) to consider the aspect of different bonding strengths and crystal structures, respectively. Using quasi-static and cyclic bending of pre-notched, unstrained micro-cantilever beams in conjunction with in-situ synchrotron X-ray diffraction the intrinsic fracture toughness ($K_{IC}$) as well as the critical failure aspects of thin films under various loading conditions are presented. Up to the high-cycle fatigue regime (*i.e.*, $N = 10^7$ cycles), the failure of monolithic sputter deposited PVD coatings is shown to be dominated by the inherent fracture resistance, irrespective of the bonding character. The recorded fatigue behaviour is further correlated with large-scale dynamic-mechanical analysis of coated Ti6Al4V platelets to step up in length scale and thus including residual stresses and changes in the elastic constants on the coating-substrate interface. The results are expected to provide key-insights into the underlying mechanisms promoting crack growth in PVD coated components.

[1] Bai, Yanyun, et al. "Stress-sensitive fatigue crack initiation mechanisms of coated titanium alloy." *Acta Materialia* 217 (2021): 117179.

**HP-ThP-5 Acoustic Monitoring of Nanoindentation Induced Nanofatigue***, **Jurgis Daugela (jdaugel1@jhu.edu)**,* Johns Hopkins University, USA*; A. Daugela,* Nanometronix LLC, USA

In the era of fast product development thin film engineers are looking for quick and efficient methods of characterization.Nanoindentation based multi-cycle loading offers an inside look into the real-time contact fracture dynamics [1]. A nanofatigue phenomenon can be observed on thin sub-micrometer films by monitoring the resulting multi-cycle nanoindentation loading-unloading curves, where post-test imaging helps identify a materials' behavior [2, 3].In addition, classical Mason-Coffin and racheting fatigue models derived for the nanoscale contact can be utilized in predictions and correlate well with experimentally obtained nanofatigue cycles.

A newly developed ultrasonic nanoindentation tip operates in the hundreds of kHz; therefore, it induces milions of load cycles within seconds.The resulting nanofatigue induces different thin film fracture modes such as radial, sink-in, and produce unique acoustic signatures.The ultrasonic nanoindentation tip monitors associated waveforms, which can provide an additional inside into the nanofatigue process dynamics via advanced acoustic waveform analysis.Following our previous study [4], acoustic waveforms were processed using a combination of wavelet based signal decomposition and Deep Learning. The proposed Deep Learning technique yields a reliable classification of acoustic signatures obtained during the fracturing of sub-micrometer thick coatings.

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**HP-ThP-6 Spotting the CSM Plasticity Error during Nanoindentation with Continuous Stiffness Measurements***, B. Merle,* Friedrich-Alexander-University Erlangen-Nürnberg (FAU), Germany*; **Hendrik Holz (hendrik.holz@fau.de)**,* University of Erlangen-Nuremberg (FAU), Germany

Dynamic nanoindentation is a popular method for continuously probing the mechanical properties of a coating as a function of depth. Here, it is shown that special caution must be exercised when testing materials with high modulus-to-hardness ratios (E/H) at fast loading rates, as the choice of harmonic parameters can result in a significant underestimation of the elastic modulus and overestimation of hardness.The errors are caused by the processing of elastic-plastic data by the lock-in amplifier in a technique initially designed to be applied to elastic deformation only. Intuitively, the higher the amount of plastic deformation within a cycle is, the larger the difference to the ideal condition is, and the higher the error is. The exact mechanisms leading to this error are discussed based on simulated CSM signals and experimental measurements.

**HP-ThP-7 Advanced Characterisation in Amorphous Thin Films for Biomedical Applications***, M. Sebastiani, **Edoardo M. Rossi (edoardo.rossi@uniroma3.it)**,* Università degli studi Roma Tre, Italy

One of the main goals of tissue engineering is the preparation of multifunctional biomaterials showing good mechanical properties, biocompatibility, and antibacterial activity simultaneously. Multi-element thin films are a new class of nano-engineered materials showing an excellent combination of high-strength and biocompatibility. Additions of Au, Cu, Zn or Ag to Ti-based films can induce potential antibacterial behavior [1, 2]. In this framework, Ti-Cu and Ti-Cu-Ag thin films were deposited on silicon substrate by physical vapor deposition magnetron sputtering (MS-PVD), with the aim of obtaining concurrent biocompatibility and antibacterial properties with better mechanical properties. The produced films were characterized by X-ray diffraction (XRD), nanoindentation, atomic force microscopy (AFM), scratch adhesion and X-ray photoelectron spectroscopy (XPS), to investigate their structural, mechanical, and surface properties. The biocompatibility of thin films is investigated by fibroblasts MRC-5 cell lines. Finally, the antibacterial activity of these thin films against Pseudomonas aeruginosa (P. aeruginosa) and Staphylococcus aureus (S. aureus) is evaluated and correlated to the Ag contents. Ti-Cu thin films shows complete amorphous structure, but addition of silver changes the film structure to partially crystalline at 20% Ag and completely crystalline at 30% Ag. XPS spectroscopy shows titanium oxidized to Ti (IV), copper partially oxidized to Cu (II) and partially in metallic state while silver remains unoxidized. The observed surface chemistry can be a main explanation for the excellent combination between biocompatibility and antibacterial properties [3]. In fact, the formation of mixed copper and titanium oxide on the surface of Ti-Cu and Ti-Cu-Ag thin films induces high biocompatibility and remarkable antibacterial properties.

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**HP-ThP-8 Capabilities of Time-of-Flight Low-Energy Ion Scattering Demonstrated on the Example of Surface Oxidation of Ti and Ti-Based Hard Coatings***, Philipp M. Wolf (philipp.wolf@physics.uu.se),* Department of Physics and Astronomy, Uppsala University, Sweden*; D. Neuß,* Materials Chemistry, RWTH Aachen University, Germany*; T. Tran,* Department of Physics and Astronomy, Uppsala University, Sweden*; M. Hans, J. Schneider,* Materials Chemistry, RWTH Aachen University, Germany*; D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden

Ion scattering methods, especially Rutherford backscattering spectrometry (RBS) and elastic recoil detection analysis (ERDA), are well established methods allowing the study of composition and structure of materials with a nm resolution. Ever thinner films and the study of surfaces introduce the need for a sub-nm resolution, difficult to achieve with MeV ion methods like RBS and ERDA. Here, we present a time-of-flight low-energy ion scattering (ToF–LEIS) setup, offering resolutions down to a monolayer,[1] using the exemplary case of surface oxidation of pure Ti and Ti-based hard coatings like TiN and (Ti,Al)N. The employed ToF-LEIS setup, able of detecting both neutrals and ions, offers high surface sensitivity to study the structure and composition of the outermost atomic layers by using primary ions with energies of 1–10 keV.[2] A connected preparation chamber, including an ion sputter gun, a heating filament, a gas inlet system, an Auger electron spectrometer (AES), a low-energy electron diffraction setup and an $e^-$–beam evaporator enables the in situ preparation and study of surfaces exposed to stimuli like high temperatures or reactive gases. The possibility of studying initial modification steps at surfaces not only offers further insights into the behavior of the immediate surface region, but can also yield knowledge on the general behavior of material systems. Due to the low ion currents necessary, ToF-LEIS, like other ion scattering methods, can be considered as non-destructive.

We demonstrate the analytical power of our approach by studying the surface oxidation of in situ grown Ti as well as ex situ grown Ti, TiN and (Ti,Al)N prepared by sputter deposition. These systems were chosen to compare surfaces more prone to oxidation like pure Ti with surfaces that show a comparably increased stability towards oxidation like TiN and (Ti,Al)N. The films were exposed to $O_2$ at pressures of $1.0\times10^{-6}$ and $1.0\times10^{-5}$ mbar for up to 90 min with sample temperatures ranging from room temperature up to 850°C. As expected, the ex situ grown Ti-based hard coatings show a high resistance to further surface oxidation even at increased temperatures, while for pure Ti we were able to observe surface oxidation both in AES and ToF-LEIS measurements already when offering $1.0\times10^{-6}$ mbar $O_2$ for 30 min at room temperature, further increasing with the amount of offered $O_2$. The presented results showcase the capability of our ToF-LEIS setup to study surfaces and ultrathin films and the effects external stimuli have on them.

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