Protective and High-temperature Coatings
Room Town & Country D - Session MA3-3-TuM

Hard and Nanostructured Coatings III

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8:20am **MA3-3-TuM-2 Magnetron Sputtered $Cr_{1-x}Ta_x$ Coatings**, ***Jan-Ove Söhngen (jan-ove.soehngen@kit.edu)**, V. Ott, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Refractory alloy thin films can exhibit unique properties which make them suitable candidates in high temperature applications. The model system chosen for our study is Cr-Ta. $Cr_{1-x}Ta_x$ coatings with various Ta contents weresynthesized by magnetron sputtering utilizing acombinatorial experiment in thin film deposition. We used a segmented circular target consisting of two half plates of pure Cr and Ta for the deposition at 250 W DC target power, 0.4 Pa Argon pressure, 0 V substrate bias and ≈ 150°C substrate temperature. Polished steel substrate samples of 10x10x1 mm^3 were placed in a horizontal line opposite to the target. Thus, we obtained different $Cr_{1-x}Ta_x$ coatings with various Ta content in a single deposition experiment.

The amount of Cr and Ta determined by electron micro analyses was used to classify the XRD (X-Ray diffraction) results:

1. All coatings are crystalline.
2. The XRD reflections of the coatings with Ta content between 15.3 at.% and 39.7 at.% exhibit similar shape and suggest these coatings are polycrystalline and grow in a single-phase bcc (body centered cubic) solid solution structure.
3. In contrast to the coatings with a lower amount of Ta, the XRD reflections of coatings with 68.5 at.% Ta content show a broader (110)-signal, indicating a much smaller crystal size and the (110) reflection of the coating with 80 at.% Ta exhibits a sharp reflection near the position of the (110)–reflection of the bcc structure and a broader shoulder, suggesting an overlap of different reflections.

This indicates a transition in the microstructure of the coatings with increasing Ta content. No intermetallic phase $TaCr_2$ was found in any of these coatings. Pure crystalline Ta coatings were not bcc structured. Transmission electron microscopy analyses will resolve the microstructure further.

Mechanical properties of the coatings were studied by micro-indentation. The hardness and Young`s modulus of the $Cr_{1-x}Ta_x$ coatings in dependence of their Ta content and as well of the pure Cr and Ta coatings will be discussed. Due to solid solution strengthening, the Vickers hardness of the $Cr_{1-x}Ta_x$ coatings exhibits a local maximum in relation with the Ta content.

8:40am **MA3-3-TuM-3 Overview and Trends in Application Driven Developments of Wear Resistant Coatings**, ***Denis Kurapov (denis.kurapov@oerlikon.com)**,* Oerlikon Surface Solutions AG Pfäffikon, Zweigniederlassung Balzers, Liechtenstein **INVITED**

The long history of the wear protective coating deposited by physical vapour deposition (PVD) technology starts more than 40 year ago from the coatings applied on cutting and forming tools. During the last years the requirements on the wear resistance in tooling industry getting more and more demanding giving strong impulses for development of new surface solutions and deposition technologies.

With significantly increased level of requirements on the performance of the wear protective coatings the development of new solutions goes more and more into direction of tailored solutions. Development of such solutions based on understanding of the wear mechanisms and correlation between coating properties and its performance. Deposition technologies need to be developed in the way to enable deposition of the coatings with desired properties.

In this paper we present an overview of the latest developments of surface solutions and PVD technologies. The main focus put on history and resent advances in development of wear protective coatings as well as on progress in arc evaporation and magnetron sputtering deposition technologies.

9:20am **MA3-3-TuM-5 Enhancing the Thermal Stability and Cutting Performance of fcc-AlCrN by Oxygen Incorporation**, *A. Michau,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; ***Tomasz Wojcik (tomasz.wojcik@tuwien.ac.at)**, P. Kutrowatz,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria; *D. Kurapov,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *H. Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

Protective coatings applied in advanced machining processes typically encounter extreme thermo-mechanical loads easily exceeding temperatures above 1000 °C. In this context, the thermal stability and, hence, the decomposition behaviour of the applied coatings is still the key-parameter for enhanced durability. Recent studies on oxygen incorporation in (Ti,Al)(O,N) highlighted the potential of defect-engineered meta-stable structures, as for the formation of wurtzite AlN domains, the non-metal mobility is decisive in the shared oxygen/nitrogen sublattice. Here, relatively small amounts of oxygen are efficient to double the required energy to form w-AlN out of $(Ti,Al)(O_xN_{1-x})$ compared to (Ti,Al)N.

Based on these results, we thoroughly investigated the decomposition behaviour of oxygen-doped $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ coatings grown by arc evaporation. During the reactive growth, the oxygen was incorporated by varying the flow rates between 15 to 70 sccm compared to 940 to 990 sccm nitrogen (p_{dep} around 4 Pa). All coatings were grown using an Oerlikon Balzers INNOVENTA kila equipped with AlCr 70/30 targets. These variations lead to purely fcc structured $Al_{0.70}Cr_{0.30}(O_{1-x}N_x)$ coatings obtaining as-deposited hardness values of 40 ± 2 GPa. The decomposition behaviour was investigated in tailormade vacuum annealing treatments (T_{an} = 700 to 1200 °C) as well as cutting tests, clearly indicating enhanced stability for the oxygen-containing coatings. The detailed phase decomposition process was investigated by transmission electron microscopy (TEM) using selected area electron diffraction, energy-dispersive x-ray spectroscopy, and high resolution TEM. The incorporation of oxygen delays the fcc to w-AlN transition from at least 800 to 1000 °C, which correlates with the results observed in the cutting tests. In more detail, crater and flank wear formation and progression are clearly delayed during wet and dry milling operations. In summary, this study highlights the potential of defect engineering via oxygen incorporation, enhancing the thermal stability of metastable fcc-structured AlCrN based coatings. In contrast to metal alloying approaches, the non-metal sublattice adaption is a simple but highly effective way to tune the properties of well-established nitrides.

9:40am **MA3-3-TuM-6 Enhancing Toughness in Nanocomposite AlCrSiN Thin Films by Crack Deflection at Sublayers: Correlating Microstructure and Micromechanical Properties**, ***Kevin Kutlesa (kevin.kutlesa@unileoben.ac.at)**, M. Meindlhumer,* Montanuniversität Leoben, Austria; *A. Lassnig,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria; *R. Daniel,* Montanuniversität Leoben, Austria; *A. Medjahed,* ESRF, France; *J. Keckes, M. Tkadletz,* Montanuniversität Leoben, Austria

Wear-resistant transition metal nitride (TMN) thin films are recognized for their exceptional hardness, high Young's modulus, superior thermal stability and oxidation resistance. However, their application is often limited by their brittleness leading to a low fracture toughness. This contribution presents a design approach encompassing (i) a nanocomposite AlCrSiN microstructure, (ii) a multilayer architecture reinforced with (iii) precisely controlled precipitation within targeted sublayers. The objective is to enhance the toughness of TMN thin films while preserving high hardness and other functional properties.

Cathodic arc evaporation was used to deposit two reference monolithic thin films, namely $Al_{0.63}Cr_{0.27}Si_{0.1}N$ and $Al_{0.675}Cr_{0.075}Si_{0.25}N$, along with a multilayer thin film consisting of alternating sublayers of these two materials. A carefully adjusted vacuum heat-treatment at 1050°C for 5 min was applied to tailor the microstructure through precipitation. Qualitative analysis of the heat-treatment's impact on thin film microstructure was conducted using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Additionally, insights into the assembly and elemental distribution in the nanocomposite microstructure were obtained through energy-dispersive X-ray spectroscopy in TEM. Cross-sectional synchrotron X-ray nanodiffraction (CSnanoXRD) at the ID13 beamline of ESRF in Grenoble facilitated the correlation of cross-sectional variations in phases, texture, microstructure, and residual stresses with the architecture and thermal history of the thin films. The nanoscale characterization revealed a nanocomposite microstructure composed of cubic Cr(Al)N and wurtzite Al(Cr)N nanocrystals with sizes of ~5 nm. In the material with lower Si content the heat-treatment induced the precipitation of cubic Cr(Al)N, while in the higher Si content material precipitation was effectively suppressed. Consequently, in the heat-treated multilayer a cross-sectional alternation of sublayers with significant precipitation and sublayers devoid of any precipitation was observed. Mechanical properties were assessed through *in situ* bending tests on freestanding microcantilevers prepared by focussed ion beam milling. The Young's modulus, fracture stress and fracture toughness were determined by loading up to fracture unnotched and notched cantilevers, respectively. A stepwise crack-propagation was observed in the heat-treated multilayer, revealing an unprecedented extrinsic toughening mechanism that significantly improved the fracture response.

10:00am **MA3-3-TuM-7 Mechanical Properties and Tribological Performance of AlCrMoN/TiSiN Nanostructured Multilayer Coatings***,* ***Ming-Xun Yang (u6au6vmp711@gmail.com)****, Y. Chang,* National Formosa University, Taiwan

A TiSiN coating with a nanocomposite structure where TiN grains are surrounded by a SiN_x matrix possesses excellent mechanical properties and make it a promising selection for wear protection of cutting tools in machining applications. However, TiSiN coatings suffer from high residual stresses and thus limit the tribological performance and hinder high temperature applications of monolithic TiSiN coatings. Recently, Mo-containing AlCrMoN coatings have received widespread attention because of improved tribological performance and toughness. In this study, the mechanical and tribological properties of AlCrMoN/TiSiN coatings with different modulation geometries, namely modulation period and modulation ratio were elaborated. During the coating process of AlCrMoN/TiSiN, CrMoN was deposited as an interlayer to enhance adhesion strength between the coatings and substrates. An impact fatigue test using a cyclic loading device and ball-on-disc wear tests at room temperature and 500 °C were conducted to evaluate the correlation between tribological properties and coating structures of the deposited coatings. X-ray diffraction (XRD) was used to characterize the microstructure, phase identification and residual stress. The microstructure of the deposited coatings was characterized by using a field emission scanning electron microscope (FESEM) and a high-resolution transmission electron microscope (HRTEM). A Rockwell indentation tester and a scratch tester were used to evaluate the adhesion strength between the coating and the substrate. The coating hardness and the elastic modulus were measured by nanoindentation. The addition of AlCrMoN into TiSiN to form a multilayer architecture provides an alternative for a hard-and-lubricious coating. The design of gradient-and-multilayered AlCrMoN/TiSiN coatings is anticipated to be advantageous in applications to enhance the mechanical properties and wear performance of mechanical parts and cutting tools.

10:20am **MA3-3-TuM-8 Influence of Deposition Pressure and Gas Mixture on the Microstructure and Phase Composition of Arc Evaporated TiSiN Coatings***,* ***Nina Schalk (nina.schalk@unileoben.ac.at)****, Y. Moritz, G. Nayak, D. Holec,* Montanuniversität Leoben, Austria*; C. Hugenschmidt,* Technical University of Munich, Germany*; V. Burwitz,* Technical University Munich, Germany*; L. Mathes,* Technical University of Munich, Germany*; C. Saringer,* Montanuniversitat Leoben, Austria*; C. Czettl, M. Pohler,* CERATIZIT Austria GmbH, Austria*; M. Tkadletz,* Montanuniversitat Leoben, Austria

Owing to their advantageous properties including excellent hardness and high oxidation stability, arc evaporated TiSiN coatings are frequently used as protective hard coatings for various machining applications in the metal cutting industry. Within this work, the influence of a varying N_2 deposition pressure and the addition of Ar to the deposition atmosphere on the microstructure and phase composition of TiSiN coatings was studied in detail. All coatings exhibited a feather-like and fine-grained structure and showed an amorphous SiN_x phase fraction. Further investigation of powdered TiSiN coatings revealed a significant decrease of the lattice parameter with increasing N_2 deposition pressure, while the elemental composition was identical for all coatings. Consequently, the changes of the lattice parameter can either be attributed to the formation of a TiSiN solid solution and/or to the formation of vacancies during the deposition process. Neither atom probe tomography nor Doppler position annihilation broadening could unambiguously clarify the presence of either a TiSiN solid solution or vacancies. Thus, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the evolution of the lattice parameter at elevated temperatures, which suggests that at lower temperatures vacancies are annihilated and then at higher temperatures Si diffuses out of the TiSiN solid solution. The coating synthesized at the lowest pressure and the one grown in a mixed N_2 and Ar atmosphere already reached the lattice parameter of pure TiN after the high temperature XRD experiment, while for the coatings grown at higher pressures an additional annealing treatment was necessary to reach this value, which might indicate that more Si is incorporated into the TiSiN solid solution at higher deposition pressures and that the additional kinetic activation stemming from the Ar ions results in less Si incorporation. The assumption that at lower annealing temperatures defects are annihilated and at higher temperatures Si diffuses out of the solid solution could be corroborated by differential scanning calorimetry and complimentary investigations of annealed coatings on substrates using energy dispersive X-ray spectroscopy and atom probe tomography. Density Functional Theory (DFT) calculations indicate that defects only play a subordinate role for the low observed lattice parameters in as-deposited state and that the addition of Ar to the deposition atmosphere results in a different incorporation of Si into the TiSiN solid solution.

10:40am **MA3-3-TuM-9 Enhanced Mechanical Properties and Thermal Stability of Novel Nanocrystalline AlNi / Al_2O_3 Multi-layered Coatings Deposited by a Combined Physical Vapour Deposition and Atomic Layer Deposition Approach***,* ***Hendrik Constantin Jansen (hendrik.jansen@empa.ch)****, B. Putz, A. Sharma,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; M. Hans,* RWTH Aachen University, Germany*; S. Lellig,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland, RWTH Aachen University, Germany*; J. Schneider,* RWTH Aachen University, Germany*; J. Schwiedrzik, J. Michler,* EMPA (Swiss Federal Laboratories for Materials Science and Technology), Switzerland*; T. Edwards,* NIMS (National Institute for Materials Science), Japan

A one-chamber-design combining physical vapour deposition (PVD) and atomic layer deposition (ALD) without breaking vacuum allows deposition of Al coatings with Al_2O_3 interlayers. These novel Al coatings possess enhanced thermal stability and mechanical properties compared to their pure PVD nanocrystalline counter-parts.
Further recent advances involve multi-layered $Al_{98}Ni_2$ / Al_2O_3 and $Al_{95}Ni_5$ / Al_2O3 (25 / 1 nm) coatings as well as their respective pure $Al_{98}Ni_2$ and $Al_{95}Ni_5$ PVD counterparts, which were deposited to evaluate the influence of grain boundary complexion engineering and the unique crystalline / amorphous interface on mechanical properties and thermal stability. The coatings were annealed at 160°C and 210°C to allow not only grain growth but also segregation enrichment at grain boundaries and triple junctions. Subsequently, microstructural stability was investigated based on lateral grain growth by X-Ray Diffraction χ-scanning and GIWAXS – out-of-plane Al grain size being limited by the 1 nm Al_2O_3 interlayers. Mechanical testing by both nanoindentation and micropillar compression at multiple strain rates allowed mechanical property analysis of the high-strength AlNi / Al_2O_3 multilayer coatings, which reached a yield strength of more than 1.3 GPa, outperforming a previously reported Al / Al_2O_3 (25 / 1 nm) coating achieving 1 GPa. Ultimately, high-resolution analyses by trans-mission electron microscopy and atom probe tomography allowed the enhanced properties to be linked to both grain boundary decoration and secondary phases that hinder dislocation and grain boundary movement.

Author Index

Bold page numbers indicate presenter