Hard Coatings and Vapor Deposition Technologies
Room Town & Country D - Session B4-1-MoM

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Naureen Ghafoor, Linköping University, Sweden, **Johan Nyman**, Linköping Univ., IFM, Thin Film Physics Div., Sweden, **Justinas Palisaitis**, Linköping Univ., IFM, Thin Film Physics Div., Sweden

10:00am **B4-1-MoM-1 Cathodic Arc Deposition of Chromium Based Coatings*, Johan Nyman (johan.nyman@liu.se)*,** *H. Högberg,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Chromium is a widely used metal in coating industry with applications as decorative coating and for wear resistant purposes. The dominating Cr coating technique has been and still is electroplating. As health- and environmental concerns of electroplating is receiving ever increased attention, a need arises to develop alternative methods of synthesizing equally well-performing coatings. The multitude of application areas for electroplated Cr means that no universal solution exists to replace it. We investigate cathodic arc deposition of metallic Cr as well as Cr-based coatings alloyed with C and/or N with the purpose to tailor the properties of the coating between metallic and ceramic, seeking a combination of hardness and toughness. Thus, focus is put on determining synthesis-composition-structure relationships and their connection to the resulting mechanical properties of the coatings. We employ nanoindentation to analyze the mechanical properties of the coatings. From applied depositions conditions, transitions between metallic and ceramic properties are identified by determining chemical compositions by Time-of-Flight Elastic Recoil Detection Analysis (ToF-ERDA), bonding structure by X-ray Photoelectron Spectroscopy (XPS), resistivity by four-point probe measurements and phase distribution by X-ray diffraction (XRD) θ/2θ scans.

For Cr-C coatings, ToF-ERDA measurements show an increase in C content from 2 at.% at a C_2H_2 partial pressure of 0.1 Pa to 40 at.% at a C_2H_2 partial pressure of 0.3 Pa, corresponding to a composition of Cr_3C_2. The increase in C content is accompanied by a decrease in deposition rate from 130 to 30 nm/min. In θ/2θ XRD scans, Cr 110, 200, 211 and 220 peaks are clearly visible at C contents below 2 at.% , but where the peak intensities are suppressed with increasing C content. At a C content of 40 at.% there are no discernable peaks, indicating growth of X-ray amorphous coatings. Four-point probe measurements confirm the metallic properties at C contents below 2 at.% where resistivity values are close to values for pure metal Cr coatings with 20 μΩ*cm. At a C content of 7 at.% the resistivity has risen to 35 μΩ*cm and at 40 at.% it is 120 μΩ*cm . Nanoindentation reveals an increase in hardness from about 8 GPa for metallic Cr to 12 GPa already at 2 at.% C, indicating that a window exists for combining beneficial properties from that of a metal and a ceramic. Results from coatings alloyed with N will also be presented.

10:40am **B4-1-MoM-3 Grain Boundary Segregation Engineering in AlCrN Hard Coatings by CrN precipitation*, Tobias Ziegelwanger (tobias.ziegelwanger@unileoben.ac.at)*,** *N. Jaeger, C. Mitterer, R. Daniel, J. Keckes, M. Meindlhumer,* Montanuniversität Leoben, Austria

As the modern day race for higher efficiency and machining speed in metal cutting industry asks for steady improvement of both hardness and toughness, this contribution has investigated grain boundary segregation engineering as a viable tool for hard coatings. Wurtzite (w-) AlCrN was chosen as a material of interest due to its favourable decomposition route and precipitation of cubic (c-) CrN. This behaviour was manipulated by alloying with Si in varying content.

A gradient coating $(Al_{0.8}Cr_{0.2})_{1-x}Si_xN$ was deposited by cathodic arc evaporation and annealed at several dedicated temperatures of up to 1100 °C. The Si content was increased with the increasing film thickness. The coating was characterized, in as-deposited and annealed states, by cross sectional X-ray nanodiffraction (CSnanoXRD), in small angle X-ray scattering (SAXS) as well as wide angle X-ray scattering (WAXS) geometries, at the synchrotron source PETRA III at the German Synchrotron (DESY) [Fig1.]. Therein, the formation of a w-AlCrN phase as well as the precipitation of c-CrN was indicated. Furthermore, the formation of periodic nanolayers within the coating in as-deposited state was observed. Their periodicities of 12 and 25 nm, depending on the Si content, were retrieved by the SAXS data.

The collected data from the gradient coating was used for the design of two multilayered coatings each consisting of alternating layers with compositions of $Al_{0,8}Cr_{0,2}N$ and $(Al_{0,7}Cr_{0,3})_{0,9}Si_{0,1}N$ in different layer thicknesses. Additionally, reference coatings of the sublayer materials were deposited as well. The mechanical properties of these four coatings were investigated by in-situ cantilever bending experiments and fracture surface analysis. The multilayered coatings displayed an increase in fracture stress of up to 20% and stable levels of fracture toughness after annealing at 1050°C. A maximum fracture stress of 4.7 GPa and fracture toughness values of 2.7 $MPam^{1/2}$ were measured.

In total it could be shown that the addition of Si to the AlCrN coating enhances its mechanical performance by change of fracture mode. However, the fracture stress did not preserve after heating at 1050°C. The multilayered coatings performed in as-deposited state between the two reference coatings, but exhibited the improved fracture stress after the heat treatment.

11:00am **B4-1-MoM-4 Influence of Deposition Pressure and Gas Mixture on the Microstructure, Phase Composition and Thermal Stability of Arc Evaporated TiSiN Coatings*, Yvonne Moritz (yvonne.moritz@unileoben.ac.at)* [1]**, *C. Saringer,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität Leoben, Austria*; M. Tkadletz,* Department of Materials Science, Montanuniversität Leoben, Austria*; C. Czettl, M. Pohler,* Ceratizit Austria GmbH, Austria*; N. Schalk,* Christian Doppler Laboratory for Advanced Coated Cutting Tools at the Department of Materials Science, Montanuniversität 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. By varying the deposition conditions, microstructural changes and thus also changes of the mechanical or thermal properties can be obtained. 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 thermal stability of TiSiN coatings was studied in detail. Scanning electron microscopy and high-resolution scanning transmission electron microscopy investigations revealed a feather-like and fine-grained structure as well as the presence of an amorphous SiN_x phase for all TiSiN coatings. However, at higher N_2 deposition pressures also several larger grains appear. Further investigation of powdered TiSiN coatings by X-ray diffraction (XRD) revealed a significant decrease in lattice parameter for an increasing N_2 deposition pressure, while maintaining an identical chemical composition. These changes in 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. In addition, the powdered TiSiN coatings were studied by *in-situ* XRD in vacuum up to 1200 °C in order to gain insight into the thermal stability of the coatings. Continuous monitoring of the lattice parameter over the whole temperature range by sequential Rietveld refinement revealed non-linear changes of the lattice parameter upon heating, resulting in a significantly larger lattice parameter for all powdered coatings after annealing. This change in lattice parameter becomes even more pronounced at higher N_2 deposition pressure. It can be assumed that this observation is an effect of Si diffusion out of the crystalline lattice during the annealing process and/or annihilation of vacancies. In order to differentiate between these two effects positron annihilation measurements were performed to evaluate if significantly different vacancy concentrations can be detected for the TiSiN samples deposited at varying N_2 pressure or in Ar/N_2 atmosphere. The presented combination of sophisticated characterization techniques contributed to gain a deeper insight into the microstructure and phase composition of TiSiN coatings synthesized with varying deposition conditions in the as-deposited state as well as at elevated temperatures.

[1] **Graduate Student Award Finalist**

11:20am **B4-1-MoM-5 Grain Boundary Segregation Alters the Fracture Mechanism of an AlCrN Thin Film**,

Michael Meindlhumer (michael.meindlhumer@unileoben.ac.at), *T. Ziegelwanger,* Montanuniversität Leoben, Austria*; J. Zalesak,* Austrian Academy of Sciences, Leoben, Austria*; M. Hans,* RWTH Aachen University, Germany*; L. Löfler, S. Spor, N. Jäger,* Montanuniversität Leoben, Austria*; A. Stark,* Helmholtz-Zentrum Geesthacht, Centre for Materials and Coastal Research, Geesthacht, Germany*; H. Hruby,* voestalpine eifeler Vacotec GmbH, Düsseldorf, Germany*; D. Holec,* Montanuniversität Leoben, Austria*; J. Schneider,* RWTH Aachen University, Germany*; C. Mitterer, R. Daniel, J. Keckes,* Montanuniversität Leoben, Austria

Despite having superior hardness and indentation modulus, thin films deposited by physical vapour deposition often lack sufficient fracture strength and toughness, which is related to intercrystalline fracture occurring predominantly along columnar grain boundaries of low cohesive energy. In this study, an $Al_{0.9}Cr_{0.1}N$ thin film was deposited by cathodic arc evaporation and thoroughly investigated. In as-deposited state, a chemical composition modulation within the wurtzite AlCrN grains was detected by transmission electron microscopy and atom probe tomography, where the Al content depleted down to ~0.83, while the Cr-content nearly doubled up to ~0.17 without interrupting the crystallographic structure. These composition modulations exhibited a periodicity of ~35 nm. A heat treatment monitored by *in situ* high-energy high-temperature grazing incidence transmission X-ray diffraction was performed on the $Al_{0.9}Cr_{0.1}N$ film. The heat treatment caused dissolution and promoted the formation of globular cubic (c) Cr(Al)N and elongated c-CrN precipitates with sizes of ~5-30 nm at the position of the former Al-content minima within the grains and at the grain boundaries, respectively, resolved by transmission electron microscopy and atom probe tomography. Additionally, some precipitations of c-Cr were found, which were attributed to macrodefects originating from the arc evaporation process. The X-ray data obtained during the heat treatment partly illuminated the segregation and formation of precipitates along the interlayer interfaces. *In situ* micromechanical testing before and after the heat treatment revealed simultaneous enhancement of Young's modulus, fracture stress and fracture toughness, most prominent enhancing fracture stress from 3.4±0.4 GPa to 5.1±0.4 GPa. Together with the strengthening of the film's mechanical properties, the fracture morphology altered from (typical) intercrystalline to transcrystalline fracture, proving enhanced grain boundary cohesion. The experimental results represent a new and cost-effective way to increase mechanical properties and thus reliability of transition metal nitride thin films.

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