Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B5-1

Hard and Multifunctional Nanostructured Coatings

Moderators: Jiri Capek, University of West Bohemia, Helmut Riedl, TU Wien, Institute of Materials Science and Technology

10:00am **B5-1-1 Effect of Boron on the Mechanical Properties, especially Fracture Toughness, of TiN**, ***Rainer Hahn,*** CDL-AOS at TU Wien, Austria*; M Bartosik, A Tymoszuk,* TU Wien, Austria*; P Polcik,* Plansee Composite Materials GmbH, Germany*; M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Mayrhofer,* TU Wien, Austria

Titanium Nitride (TiN) thin films pioneered the application of ceramic hard coatings on tool materials for improving the wear resistance and consequently tool lifetime. The enhancement in wear resistance strongly depends on the mechanical properties of the coating, which can be further increased by alloying strategies. Here, we present the effect of boron alloying to TiN hard coatings on their mechanical properties, with a focus on the fracture toughness (K_{IC}).

Thin films with different boron contents, ranging from 0.5 to 25 at%, were deposited using reactive, as well as non-reactive, unbalanced magnetron sputtering. The boron content and bonding characteristics (different types of B-bonds) were analysed by X-ray photoelectron spectroscopy and complemented by X-ray diffraction experiments to gather information on the structure of our hard coatings. The experiments unveil a clear increase in B-N-typed bonds with increasing boron content, resulting in a transition from fine-grained single-phase Ti(B)N (up to a B content of around 5 at%) to nanocrystalline two-phase Ti(B)N-BN structures (for contents >5 at%).

Micromechanical experiments ---------—conventional nanoindentation as well as fracture experiments— reveal hardnesses of up to 32 GPa and fracture toughness values of up to 11 MPa√m (both values include the influence of pronounced residual stresses in the coatings on Si (100) substrates) for boron contents of up to 5 at%. Higher boron contents resulted in a decrease in fracture toughness, hardness, and indentation modulus. We envision a soft, X-ray amorphous BN phase surrounding nanocrystalline TiN grains, to be responsible for this behaviour.

Based on our results we can conclude that B alloying has the potential to boost the mechanical properties of nitride based hard coating materials but only when softer BN phases are avoided, which can be controlled by carefully adapting the deposition parameters.

10:20am **B5-1-2 Evolution of Structure, Residual Stresses and Wear Resistance of Multi-layered AlTiSiN-AlCrN Coatings upon Thermal Loading Revealed by Cross-sectional X-ray Diffraction and Tribological Testing**, ***Stefan Klima,*** *N Jäger, M Meindlhumer,* Montanuniversität Leoben, Austria*; H Hruby,* eifeler-Vacotec GmbH, Germany*; C Mitterer, J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Multilayered nanocrystalline coatings typically differ in terms of microstructure (phase, texture, size and shape of grains), residual stresses and mechanical properties with respect to their monolithic counterparts due to specific size restrictions, altered growth conditions and effect of the interfaces. This allows an application-relevant optimization of microstructure-dependent coating properties by a specific coating architecture prepared under optimized deposition conditions. In order to understand the complex structure-stress-property relations in hierarchical nanostructured coatings, a multi-layered multi-phase AlN-based coating system was developed and studied by cross-sectional position-resolved synchrotron X-ray nanodiffraction in transmission geometry, nanoindentation and tribological testing. The specially designed coating architecture was analyzed in the as-deposited state and after thermal treatment, with a special focus on the thermo-mechanical properties and oxidation resistance. In this system, AlTiSiN and AlCrN layers were combined with a specific focus on the role of structure confinement by the multi-layered architecture for varied thicknesses of individual layer components. This approach allowed studying the effect of inherent structure (phase, texture, size and shape of grains), number of interfaces and residual stress distribution over the coating thickness on the mechanical properties and wear. Moreover, the effect of the combination of the metastable AlTiSiN, composed of cubic, hexagonal and amorphous phases, and the stable hexagonal structure of AlCrN on the development of structure, stress state and properties was studied in detail, revealing complex depth-evolutions of phases, texture, grain size and residual stresses. Furthermore, the particular coating structures of the complex multi-layered system were individually tested under various tribological conditions such as counterpart materials, annealing conditions and temperatures. The results document pronounced changes in the mechanical properties, thermal stability, residual stresses and wear resistance in the dependence of the coating architecture, which contributes to a general understanding of the structure-stress relationships in multi-layered films with various architectures and material combinations.

10:40am **B5-1-3 Plasma Tailoring for Controlled Compositional and Microstructural Evolution of TiB_2 Coatings from Magnetron Sputtering Techniques and DC Vacuum Arc**, ***Johanna Rosen,*** Linköping Univ., IFM, Thin Film Physics Div., Sweden*; N Nedfors, I Zhirkov,* Linköping University, IFM, Thin Film Physics Division, Sweden **INVITED**

Titanium diboride (TiB_2) is a versatile (hard) material of high potential for various thin film applications due to its combination of, e.g., high strength, high melting temperature, and high conductivity. This presentation will show paths for controlled synthesis of TiB_2 through choice of synthesis technique and drastically different (inherent) plasma properties. Starting with magnetron sputtering of TiB_x films from a TiB_2 target, it often result in highly overstoichiometric films due to differences in kinetic energy, ejection angle, and gas-phase scattering of sputtered Ti and B species. We show that the B/Ti atomic ratio can be reduced from 2.7 to 2.1 by increasing the Ar pressure from 5 mTorr to 20 mTorr, while also changing to stronger magnets in the magnetron to retain dense films of high crystal quality. High power impulse magnetron sputtering (HiPIMS) have a higher fraction of ionized sputtered species compared to regular dc magnetron sputtering, and it is possible to control the flux of ionized species by varying the pulse frequency, and hence duty cycle. This allows exploration of the effect of ion to neutral flux ratio on the coating microstructure while keeping the substrate bias potential constant. We show that the additional energy supplied during film growth in the HiPIMS process results in a change from a randomly oriented polycrystalline microstructure to a 001-textured nanocolumnar structure. The change in preferred orientation also influence the hardness, which is enhanced from 36 GPa to ≥ 42 GPa. A further increase in the ion flux to the substrate leads to denser coatings with a higher residual compressive stress. Applying a pulsed bias in synchronous with the HiPIMS pulse, the relative fractions of B^+, Ti^+ and Ar^+ within the flux of bombarding ions can be varied. This makes it possible to tune and lower the residual stress compared to coatings deposited under bombardment of mainly Ar^+ ions. Finally, we also present results from TiB_2 synthesis based on DC vacuum arc, and a new design of cathode - anode assembly allowing a stable, reproducible, and close to fully ionized plasma flux of Ti and B. The arc deposited coatings have a stoichiometry close to 2. Despite observations of macroparticle generation during synthesis, the film surface is very smooth with a negligible amount of particles.

11:20am **B5-1-5 Development of Novel Gradient C-CrAlSiN Based Cathodic Arc PVD Coatings for High Speed/dry Machining Applications**, ***Puneet Chandran,*** *V Krishna,* International Advanced Research Centre for Powder Metallurgy and New Materials (ARCI), India*; A VenuGopal,* NIT Warangal, India

High speed dry machining is gaining interest by the day especially with the increasing employment of difficult-to-machine materials in niche areas. The advantages associated with this process (high productivity, superior work quality) fall short during the machining of difficult materials due to the high wear rate and low thermal stability associated with conventional tools/coatings. Nanocomposite coatings have been employed in such cases in view of their multiple advantages such as enhanced hardness along with high thermal stability and excellent oxidation resistance. Although these coatings are considered to perform better than the conventional coatings, their functionality is reduced during high speed dry machining owing to the higher coefficient of friction. A lubricating (low coefficient of friction) layer/coating to overcome the high friction in between the mating surfaces is essential. A probable solution is the application of diamond like carbon coatings which are characterized by high hardness along with a low coefficient of friction. However, these films are plagued by extremely high compressive stresses, low thermal stability and poor substrate-coating adhesion. Thus, carbon doped nanocomposite coatings have been conceptualized to overcome the area where the diamond like carbon coatings have failed, rendering an advanced coating for high speed dry machining applications.

Optimized CrAlSiN nanocomposite coating and carbon incorporated CrAlSiN coating were deposited separately using the cylindrical cathodic arc PVD technique. The as deposited films were comprehensively analyzed to determine their adhesion strength, phase composition, friction coefficient, hardness and sliding wear properties. Preliminary observations revealed that although the films did not show evidence of DLC formation (from Raman analysis) there was a considerable decrease in the coefficient of friction with carbon content. Further, an increase in the incorporation of carbon into the optimized CrAlSiN coatings led to a steep decrease in the hardness values. This result persuaded a study on developing a novel carbon based gradient coating which would retain the properties of a nanocomposite whilst supporting the nanocomposite under-layer by reducing the coefficient of friction. The performance of the coating was evaluated based on real time machining behavior during drilling and milling on EN 24 work piece. A detailed discussion on the physical, mechanical and tribological properties of the gradient carbon based CrAlSiN coatings in relation to their wear behavior during drilling and milling will be presented in the conference.

Author Index

Bold page numbers indicate presenter