Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-4

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Chau-Chang Chou, National Taiwan Ocean University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

2:10pm **B4-4-3 Coatings Selection Criteria for WC/Co Cutting Tools**, ***Aharon Inspektor***, *P Salvador,* Carnegie Mellon University, USA **INVITED**

Internet of Things (IoT), where all objects have unique identifiers and incessant internet connectivity, will fundamentally change the world we live in and the manufacturing industry. In this paper we will examine the impact of the forthcoming 4th Industrial Revolution on machining industry, the anticipated changes in metal cutting procedures and the emerging new generation of cutting tools.

The use of embedded sensors, fast connectivity and intelligent feedback in metal cutting has the potential to increase material removal rates at significantly tougher thermal and mechanical conditions at the cutting edge. Successful implementation of the new technologies will require similar progress in cutting tools. We will first review and analyze current trends and machining strategies in leading workshops. Then, we will discuss key criteria for the design of new cutting tools, and guidelines for the development of new functional coatings. The coating selection criteria will be based on the current and on the anticipated machining wear-maps that chart the optimum machining conditions for various workpiece materials. The paper will include examples from machining High Temperature Alloys, Stainless Steel and Carbon Composites.

2:50pm **B4-4-5 Investigation of the Plasma Electrolytic Oxidation Mechanism of Titanium**, ***Golsa Mortazavi***, *E Meletis,* University of Texas at Arlington, USA

Plasma electrolytic oxidation (PEO) is an environmentally friendly technology capable of forming coatings with excellent adhesion strength. Total applied current to the oxide, in this process, is composed of electronic current caused by sparking and ionic current caused by diffusion of electrolyte ions into the oxide. Correlation between the ionic/electronic current contribution rate at different current densities and the oxide layer characteristics is utilized to understand the coating growth mechanism during the PEO stages. In this study, titania films were produced via PEO on commercially pure titanium in an alkaline phosphate electrolyte at various current densities i.e. 30, 40, 50, 60, 80, 100, and 110 mA/cm^2. Voltage-time (V-t) behavior has been investigated to elucidate the contribution of ionic and electronic current and different stages of PEO process. The V-t response showed that at low current densities, voltage attained relatively constant values, due to the dominance of the electronic current that is mainly due to sparking and as such is independent of the film resistance. High density of plasma discharge at this condition, forms large number of discharge channels and increases the porosity and surface roughness of the coating. Also, these plasma discharges provide enough energy to raise temperature facilitating formation of both rutile and anatase. At high current densities though, the ionic current dominates enhancing ionic diffusion through the oxide resulting in a dense, thick anatase film. The present results show that the V-t response can be utilized to elucidate the oxide growth mechanism during PEO process.

3:10pm **B4-4-6 Lessons Learned from Sputtering Icosahedrally Bonded Borides**, *O Hunold, P Keuter, P Bliem, D Music, F Wittmers, A Ravensburg,* RWTH Aachen University, Germany*; D Primetzhofer,* Uppsala University, Sweden*;* ***Jochen Schneider,*** RWTH Aachen University, Germany

We have systematically studied the effect of transition metal valence electron concentration (VEC) of amorphous $T_{0.75}Y_{0.75}B_{14}$ (a–$T_{0.75}Y_{0.75}B_{14}$, T= Sc, Ti, V, Y, Zr, Nb) on the elastic properties, bonding, density and electronic structure using *ab initio* molecular dynamics. As the transition metal VEC is increased in both periods, the bulk modulus increases linearly with molar- and mass density. This trend can be understood by a concomitant decrease in cohesive energy. T' = Ti and Zr were selected to validate the predicted data experimentally. A–$Ti_{0.74}Y_{0.80}B_{14}$ and a–$Zr_{0.75}Y_{0.75}B_{14}$ thin films were synthesized by high power pulsed magnetron sputtering. Chemical composition analysis revealed the presence of up to 5 at.% impurities, with O being the largest fraction. The measured Young's modulus values for a–$Ti_{0.74}Y_{0.80}B_{14}$ (301±8 GPa) and a–$Zr_{0.75}Y_{0.75}B_{14}$ (306±9 GPa) are more than 20% smaller than the predicted ones. The influence of O incorporation on the elastic properties for these selected systems was theoretically studied, exemplarily in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Based on *ab initio* data, we suggest that a–$Ti_{0.75}Y_{0.75}B_{14}$ exhibits a very dense B network, which is partly severed in a–$Ti_{0.75}Y_{0.75}B_{12.75}O_{1.25}$. Upon O incorporation, the average coordination number of B and the molar density decrease by 9% and 8%, respectively. Based on these data the more than 20% reduced Young's modulus obtained experimentally for films containing impurities compared to the calculated Young's modulus for a–$Ti_{0.75}Y_{0.75}B_{14}$ (without incorporated oxygen) can be rationalized. The presence of oxygen impurities disrupts the strong B network causing a concomitant decrease in molar density and Young's modulus. Very good agreement between the measured and calculated Young's modulus values is obtained if the presence of impurities is considered in the calculations. The implications of these findings are that prediction efforts regarding the elastic properties of amorphous borides containing oxygen impurities on the at.% level are flawed without taking the presence of impurities into account.

3:30pm **B4-4-7 Ductile Behavior of Hard MoBC and WBC Nanolaminates**, ***Petr Vašina***, *P Soucek, S Mirzaei, L Zabransky,* Masaryk University, Czech Republic*; J Bursik,* IPM, Academy of Science, Czech Republic*; V Perina,* NPI, Academy of Science, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic

State-of-art ceramic materials nowadays used as protective coatings such as TiN, TiAlN, c-BN etc. generally exhibit high hardness and high stiffness. These positive features are often accompanied by negative brittle deformation behaviour. To overcome this limitation a new generation of materials with high hardness and moderate ductility is desired. Recently, there has been an increased interest in boron and carbon based nanolaminates such as Mo_2BC [1] which exhibit a very similar structure to the MAX phases. According to the ab-initio models, these materials were predicted to exhibit unusual combination of high stiffness and moderate ductility [1]. The coatings were deposited either by DCMS at extremely high substrate temperature of 900°C [1] or at moderate temperature of 380°C employing HiPIMS [2]. In our research, co-sputtering of Mo (W), C and B_4C targets to finely tune the coating composition of Mo_2BC and W_2BC was used. Mid-frequency pulsed DC plasma excitation was employed to enhance the ion flux on the substrate by factor of 3 compared to DCMS case which promoted the crystallization of Mo_2BC. Coatings with the same XRD patterns as those deposited by HiPIMS at the same substrate temperature were prepared. The moderate deposition conditions resulted in grown of partially crystalline Mo_2BC coatings with nanocomposite structure where small Mo_2BC crystallites of approx. 10 nm size were embedded in an amorphous matrix. These coatings showed high hardness of 31.6 ± 0.8 GPa and extremely high fracture toughness – it was even impossible to form a crack in these coatings at extremely high indentation load with cube corner indenter where both the coatings and the underlying hard-metal substrate were severely plastically deformed. Only a shear/slip plane defects typical for ductile materials were detected. This required ductile behavior of hard coating observe for partially crystallite Mo_2BC with nanocomposite structure is hard to be met with other commercial coatings tested by similar manner.

1. J. Emmerlich, D. Music, M. Braun, P. Fayek, F. Munnik, J.M. Schneider, J. Phys. D: Appl. Phys, 2009 42 185406 (6pp).

3:50pm **B4-4-8 Coating Characterization with Surface Acoustic Waves**, ***Martin Zawischa***, *D Schneider, M Leonhardt, S Makowski, V Weihnacht,* Fraunhofer IWS, Germany

Measuring film properties is essential for understanding and designing coating systems and for controlling quality in coating manufacturing.

For more than ten years now, the laser-induced surface acoustic wave technique has been proven as a fast and non-destructive way to characterize coating and surface properties. Several parameters influence the velocity of the waves like Young's modulus, coating thickness, porosity, subsurface damage or hardening zone. Due to the fact, that the penetration depth of propagated waves depends on wave frequency, a bundle of information about the above mentioned parameters can be obtained from the measured dispersion curve of the detected waves. Once the dispersion curve has been measured, a physical model of the coating system is fitted to the measured data to derive the information of interest.

Fields of applications in both research and industrial environments are PVD and CVD coatings, thermal-sprayed coatings, semiconductors, low-k films and bulk materials.

Up to now, the physical model was limited to a single layer or to multilayers with two alternating materials. In this work, an implementation

of a more advanced model is presented, which accounts for up to five individual layers with full data set. By means of examples, fitting of some multi-layer systems is demonstrated. In one example several variants of a DLC coating system with a chromium interlayer deposited on a silicon wafer are measured. The number of obtainable parameters is discussed with respect to the shape of the dispersion curve. Different measurement strategies can be deduced from these finding and extend the possibilities of the laser-induced surface acoustic wave method.

4:10pm **B4-4-9 Anti-Corrosion Performance and Wear Behaviour of Laser Deposited Ni-Ti-Zn Coatings on UNS G10150 Steel.**, ***Ayanda Xulu,*** Tshwane University of Technology, South Africa*; O Fatoba,* University of Johannesburg, South Africa*; A Popoola,* Tshwane University of Technology, South Africa*; S Pityana,* Council for Scientific and Industrial Research (CSIR), South Africa

The untimely failure of engineering steels when exposed or used in harsh working environment is attributed to low hardness, poor tribological behaviour and corrosion resistance and this invariably restricting its applications. Since the durability of steel is determined by its deterioration over time which is affected by the environment, tailoring of the surface composition and microstructure through laser deposition becomes very vital. The investigation of Ti-Zn-Ni coatings by laser deposition technique is aimed at enhancing the properties of Ti-Zn-Ni coatings on UNS G10150 steel. A 3 kW continuous wave ytterbium laser system (YLS) attached to a KUKA robot which controls the movement of the deposition process was utilized for the fabrication of the coatings. The fabricated coatings were investigated for its hardness, corrosion and wear resistance performance at different laser processing parameters. The corrosion behaviour was investigated in 1M H_2SO_4 and 3.65wt.% NaCl solutions at 28°C via Electrochemical Impedance Spectroscopy (EIS) and Potentiodynamic Polarization techniques. The optical microscope (OM), field emission scanning electron microscope equipped with energy dispersive spectroscopy (SEM/EDS) were used to study the morphology of the fabricated coatings and X-ray diffractometer (XRD) for the identification of the phases present in the coatings . The improved hardness and wear resistance performance were attributed to hard Ti_2Ni intermetallic compound, martensitic TiNi and TiZ_{16} phases. The coatings were found to have uniform and fine microstructures free of cracks and pores. The enhanced corrosion resistance was also attributed to NiTi and TiO_2 phases formed.

4:30pm **B4-4-10 Effect of V Addition on the Thermal Stability, Oxidation Resistance and Tribological Performance of Self-lubricant TiSi(V)N Coatings Deposited by HiPIMS in DOMS Mode**, ***Filipe Fernandes,*** *R Serra, A Cavaleiro,* SEG-CEMUC, University of Coimbra, Portugal

Effective lubrication and wear protection at high temperature and in cyclic environments are continuing challenges that are crucial for energy efficiency in turbomachinery, machining tools and aerospace applications. In recent years, various self-lubricating coatings have been developed by combining hard and wear resistant binary or ternary coatings (such as TiN, TiAlN, CrN, CrAlN, YSZ) with specific elements (e.g. Ag, V) that reduce friction by diffusing to the surface and/or forming a low friction tribolayer on the wear surface. Despite the improvement in friction and wear resistance, the quick depletion of the lubricious specie from the coating system by rapid out diffusion and consequently loss of improved tribological behavior delayed their upscaling to the industry. A promising approach for controlling diffusion of the lubricant element is the use of a diffusion barrier layer. This is the case of the TiSiN coating system, which deposited as nanocomposite structure the amorphous Si-N phase can work as an antidiffusion barrier. Thus the aim of this work is to evaluate the effect of V additions on the structure, thermal stability, oxidation resistance and tribological performance of TiSiN films deposited with dissimilar Si contents, with emphasis on the development of selflubricant coatings with control release of the lubricious phase. TiSi(V)N coatings with different vanadium and Si contents were deposited by DOMS. Temperature effect on the structure of the V rich coating was characterized in open air in-situ by hot-XRD device in the range of 500 °C to 750 °C. Thermal stability was studied in a protective atmosphere in the range of 500 °C to 1000 °C. The oxidation behavior of coatings was studied by thermogravimetry (TGA). Bright field scan transmission electronmicroscopy STEM/EDX maps and elemental profiles along the cross section of the oxidized coatings were acquired to understand the kinetics of ions diffusion and oxide scale growth. Tribological behaviour of coatings was characterized in a high temperature tribometer. After wear tests, the wear tracks and wear debris were characterized by scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS) and Raman spectroscopy. Oxidation resistance of coatings decreased with V additions. Tribological tests showed that friction and wear rate of coatings decreased progressively with increasing vanadium content.

4:50pm **B4-4-11 Wear Study of PVD AlTiN Coatings with High Al Content**, ***Joern Kohlscheen,*** *C Bareiss,* Kennametal GmbH, Germany*; C Charlton, D Banerjee,* Kennametal Inc., USA

AlTiN coatings are widely used as protective coatings in the cutting tool industry. It is generally accepted that increasing the aluminum content from 50 to about 65 at. % (metallic fraction of the compound) improves the tool performance in many applications. However, for high hardness the coating structure needs to remain essentially cubic (fcc). If deposition parameters are not optimized or the Al content is increased further, considerable amounts of the soft hexagonal phase will be deposited and wear resistance of the film is reduced. We present a study of AlTiN coatings with compositions near an elemental ratio of 2:1 (Al:Ti). Carbides samples were coated by arc PVD using a commercial system. Phase change in the films was promoted with selected variants by annealing up to 1000 degree C under vacuum. Structural analysis was done by SEM and XRD (BB and GI mode). Basic mechanical properties were determined by universal hardness testing. The wear behavior of the coatings was studied by cyclic indentation on the macro and micro scale and the resultung wear is described in detail. As expected, aluminum contents above 65 at. % lead to rapid decrease in wear resistance. Formation of the undesired hexagonal phase could be delayed by suitable deposition parameters (magnetic field at the arc source). Annealing for extended periods of time reduce coating performance again as more hexagonal phase is formed. The wear behavior in the laboratory test generally reflects the results obtained under more complex loading situation (dry milling of ductile cast iron).

5:10pm **B4-4-12 Tribological Behavior of MoBCN-MoSx Coating under Elevated Temperature**, ***Xiaodong Zhu,*** *Q Li, L Qiu, K Xu,* Xi'an Jiaotong University, China

To extend the utilization of tribological coatings, people have designed adaptive or “chameleon” coatings which reduce friction and wear by changing surface chemistry and microstructure in response to the change of environment and loading. In these coatings, a wear-resistant phase was chosen as the main phase and some lubricating phase as assistants. The wear-resistant phase usually has a high friction and large amount of lubricant is necessary to reduce the coefficient of friction, and thus leads to low hardness and reduced oxidation resistance . MoBCN coating was found to have low friction coefficient from room temperature to 600 ℃ . By adding lubricating phases of MoS_2, the MoBCN/MoS_2 composite coating may possess better tribological propertiesfor wide temperature range.

In this study, MoBCN/MoS_x coatings were prepared by ion beam enhanced magnetron sputtering from a Mo/B_4C /MoS_x composite target. The content of boron and sulfur was controlled by the number of the corresponding mosaic targets. The friction and wear behaviors of these composite coatings were evaluated by ball-on-disc wear test at different temperatures. The introduction of sulfer reduces the coefficient of friction and wear rate at room temperature. However, it is oxidized into MoO_3 and loses its character of lubrication at elevated temperature, accordingly its oxidation tendency increases. It is shown that more content of boron may reduce the negative effect of sulfur on the oxidation resistance, and thus its tribological behavior at elevated temperature is improved. Therefore, boron is proved to be the key element in enhancing tribological performance of MoBCN/MoS_x coating at elevated temperature.

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