Hard Coatings and Vapor Deposition Technologies
Room Town & Country C - Session B1-1-ThM

PVD Coatings and Technologies I

Moderators: Dr. Christian Kalscheuer, RWTH Aachen University, Germany, **Dr. Vladimir Pankov**, National Research Council of Canada

8:00am **B1-1-ThM-1 New Challenges and Opportunities for PVD Coatings in Metal Cutting Applications**, ***Aharon Inspektor***, Carnegie Mellon University, USA **INVITED**

Many leading hard and superhard PVD coatings were developed as protective layers for cutting tools. Accordingly, the machining shop became a proving ground for testing new coatings and for the development of new concepts in materials science. In this talk, we will study how the ongoing 4th industrial revolution, with a multi-level connectivity of sensors, machines and systems and with computer controlled automated facility system, will affect the current machining routines. We will first examine the current criteria for choosing the right tool for the application, (and explain why many new coatings remain underutilized). Then we will review the basic features of Industrial Internet of Things (IIOT) revolution. And conclude by discussing how the expected changes in machining shop will affect the manufacturing landscape, change tooling criteria and likely open new opportunities for hard coated cutting tools.

8:40am **B1-1-ThM-3 Custom-Fit Hipims Coatings for Cutting Tools Used in a Wide Variety of Machining Applications**, ***Stephan Bolz***, *B. Mesic, O. Lemmer, W. Kölker, C. Schiffers,* CemeCon AG, Germany

Coated cutting tools are used in many different machining applications. One of them is heavy duty machining. In this application, high wear resistance is primarily achieved by the highest possible thickness of the protective coating. To deposit such thick layers with good adhesion around the cutting edge, their residual stress must be kept as low as possible.

Completely different machining applications are, for example, hard machining or machining of austenitic stainless steel. Here, it is preferable to go for sharp edged cutting tools in combination with a thin and very hard wear protective layer.

As different as the applications may be, the HiPIMS technology offers the most possibilities in the PVD sector to specifically adjust coating properties.

The presentation will show how we can tailor properties of HiPIMS coatings for all different applications by adjusted selection of process parameters.

9:00am **B1-1-ThM-4 Film Growth Control at Cutting Edges to Overcome Edge Rounding**, ***Otmar Zimmer***, *T. Litterst,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany*; T. Kruelle,* Technical University Dresden, Germany

Cutting edges are often coated with hard and wear resistant films. These films are typically based on metal nitrides, - oxides or – carbides. They are deposited with thin film technologies such as PVD or CVD.

Unfortunately the geometries of the cutting edges are changed by the coating, in particular the edge radius is enlarged (edge rounding). Therefore the film thickness is limited and the initial radius of the uncoated tool must be smaller than the target radius of the coated edge.

A new coating process based on vacuum arc PVD was developed to overcome this situation. By means of selected coating materials and process conditions the film growth at edges can be controlled properly within certain limits. So it is possible to grow up edge sharper than the initial edge geometry.

The potential of this coating approach is great, because the film thickness limitation will be overcome. On the other hand the coating process is simplified because the edges to be coated can have a higher radius. So adhesion issues or local overheating are avoided.

Beside the new coating process also an evaluation method for the edges stability under different load conditions was developed and used. It is based on a well defined grinding process directly at the edge. Significant differences between various coating materials were found. Also a hypothesis concerning key parameters and the mechanism of the "sharpening effect" was established. Demonstrator tools were prepared this way. Edge analyses and application tests were performed. The paper gives an overview about the technological approach, testing procedures and results and also a couple of examples.

9:20am **B1-1-ThM-5 Computational Tool for Analyzing Stress in Thin Films**, ***Eric Chason***, *T. Su, Z. Rao,* Brown University, USA

Stress in thin films can have a significant impact on performance and reliability of the devices they applied to, so there is a large motivation for understanding and controlling it.The stress is affected by many parameters (growth rate, temperature, microstructural evolution, composition, particle energy for sputter deposition, etc.) which offers numerous pathways to modify it. Over the past few years, we have developed a kinetic model that can predict the stress evolution under different conditions. This model has been incorporated into a computer program to analyze wafer curvature measurements of stress.Non-linear least squares fitting is used to determine a set of kinetic parameters that best explain the data. These parameters can then be used to predict and optimize the film stress. The program is implemented as a web-based application with associated instruction manuals to describe its use and physical basis. The program has a user-friendly interface that allows the user to customize the fitting range and which parameters are made to be common among the multiple data sets. This presentation will explain the physical basis of the model and give examples of its use.

9:40am **B1-1-ThM-6 Effect of CrAlN Coating Properties on Impact Fatigue of Tool Steel**, *K. Bobzin, C. Kalscheuer, M. Carlet,* ***Muhammad Tayyab***, Surface Engineering Institute - RWTH Aachen University, Germany

The tools in forming processes like cold forging are subjected to cyclic impact loads. Physical vapor deposition (PVD) coatings can further improve the service life of such tools given the effect of coating properties on the fatigue behavior of coated substrate is well-understood. Previous investigations on the cyclic impact loading of PVD coated tool steels mainly correlate the plastic deformation of the substrate to the resulting coating cracks and delaminations. However, the influence of coating properties in such cases needs further clarification. Therefore, the current work aims to investigate the combined effect of thickness, morphology, elastic-plastic properties and residual stress state of the coating on the impact fatigue behavior of coated tool steel substrates. For this purpose, two CrAlN coatings with Al/Cr-ratio of $x_{Al/Cr}$ = 0.12 and $x_{Al/Cr}$ = 0.52, each with a thickness of s = 1.7 µm and s = 3.5 µm, were deposited on HS6-5-2C susbstrates. The residual stresses were measured by focused ion beam-digital image correlation (FIB-DIC) ring-core method. The elastic-plastic properties of the coatings were determined by nanoindentation. The coated samples were subjected to cyclic impact testing with an initial Hertzian contact pressure p_H = ~ 9.7 GPa and frequency f = 50 Hz. The fatigue behavior was studied by analyzing the impact impressions for fatigue cracks with scanning electron microscopy after N = 0.1, 0.5 and 1 million impacts. An increase in coating thickness led to higher compressive residual stresses of σ > -3 GPa along with a decrease in indentation hardness H_{IT} of the coating. Such behavior could be attributed to a longer columnar morphology of thick coatings resulting in higher inclination and inter-columnar shearing under indentation load. This combined effect of the considered coating properties further influenced the impact fatigue as the thick coatings led to reduced resistance of coated substrates against initiation of fatigue cracks. The investigation contributes to adjusting coating thickness and resulting coating properties for higher tool service life in applications involving cyclic impact loading.

10:00am **B1-1-ThM-7 Toward Energy-efficient Physical Vapor Deposition: Routes Fordensification of $(Ti_{1-y}Al_y)_{1-x}W_xN$ Thin Films Grown with no External Heating**, ***Xiao Li***, *A. Pshyk, B. Bakhit,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; M. Johansson Jõesaar, J. Andersson,* SECO Tools AB, Sweden*; I. Petrov,* University of Illinois at Urbana, USA*; L. Hultman, G. Greczynski ,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

In view of the sustainable development goals and to satisfy the demand for growing dense, hard coatings for protecting temperature-sensitive substrates, the quest for lowering energy consumption during thin film growth by magnetron sputtering becomes of pressing importance. Here, we introduce a method which replaces thermally-driven adatom mobility, necessary to obtain high-quality fully-dense films, with that supplied by effective low-energy recoil generation resulting from high-mass metal ion irradiation of the growing film surface. This approach enables the growth of dense and hard films with no external heating at substrate temperatures T_s ≤ 130 ºC in a hybrid high-power impulse and dc magnetron co-sputtering (HiPIMS/DCMS) setup involving a high mass (m > 180 amu) HiPIMS target and metal-ion-synchronized bias pulses. Compared to conventional PVD methods, the energy savings are as much as 64%.

First, the effect of the metal ion mass on the densification, phase content, nanostructure, and mechanical properties of metastable cubic $Ti_{0.50}Al_{0.50}N$

based thin films is reviewed. Three series of $(Ti_{1-y}Al_y)_{1-x}Me_xN$ (Me = Cr, Mo, W) films are grown with *x* varied intentionally by adjusting the DCMS power. Results reveal a strong dependence of film properties on the mass of the HiPIMS-generated metal ions. All layers deposited with Cr^+ irradiation exhibit porous nanostructure, high oxygen content, and poor mechanical properties. In contrast, $(Ti_{1-y}Al_y)_{1-x}W_xN$ films are fully-dense even with the lowest W concentration tested, *x* = 0.09. We then discuss the effects of the high-mass W^+ irradiation on film properties with W^+ energy E_{W^+}(~90-630 eV, controlled by substrate bias voltage amplitude V_s) and *x* (0.02-0.12, controlled by the HiPIMS pulse length). Results reveal that a strong coupling exists between the W^+ incident energy and the minimum W concentration required to grow dense layers.We establish that dense, high-quality coatings can be obtained provided that the W^+ momentum transfer per deposited metal atom is sufficiently high. Finally, the behavior of $(Ti_{1-y}Al_y)_{1-x}W_xN$ films upon annealing in vacuum up to 1000 °C is demonstrated.

10:20am **B1-1-ThM-8 Effects of Nitrogen Contents on the Microstructure and Corrosion Resistant Evaluation of ZrTiNbSiFeNx High Entropy Alloy Coatings***, **Chen Wei-Yang**, K. Yu-Lin,* National Taiwan University of Science and Technology, Taiwan*; L. Bih-Show,* Chang Gung University, Taiwan*; L. Jyh-Wei,* Ming Chi University of Technology, Taiwan

The high entropy alloy (HEA) coatings has been widely studied since 2004 because of their unique mechanical properties, good corrosion and high temperature oxidation resistance. In this study, the nitrogen contained ZrTiNbSiFe HEA coatings were grown using a high power impulse magnetron sputtering (HiPIMS) system. Six ZrTiNbSiFeNx thin films containing different nitrogen contents were grown under different Ar to nitrogen flow rate ratios. The chemical compositions of HEA films were analyzed by a field emission electron probe microanalyzer (FE-EPMA). The crystalline structures of HEA films were evaluated by an X-ray diffractometer. The cross-sectional morphologies of HEA films were analyzed by a field emission scanning electron microscope and a transmission electron microscope. The nanoindenter, scratch tester, and pin-on-disk wear tester were employed to study the hardness, adhesion and tribological properties of each HEA film, respectively. Effects of Ar to nitrogen flow rate ratios and nitrogen contents on the phase, microstructure, and mechanical properties of ZrTiNbSiFeNx thin films were explored in this work ,The polarization curve and surface corrosion morphology of the film in 3.5 wt.% sodium chloride aqueous solution were tested by a potentiostat, and it was found that the corrosion resistance of the film was better than that of 304 SS.

10:40am **B1-1-ThM-9 Development of a Multilayer Ti/TiN/TiAlN/ReN Coating System and Evaluation of their Microstructural, Mechanical and Tribological Properties***, **Hernán Darío Mejía Vásquez**, G. Bejarano Gaitán,* University of Antioquia, Colombia

The need to improve the wear resistance of hot work steels in applications such as injection and extrusion of aluminum alloys, and high-speed steels for machining different parts in manufacturing processes, have led to the development of new materials in the form of coatings. With the purpose of improving the wear resistance of the M2 high-speed steel, a multilayer coating system consisting of 1, 10, 20, 30 and 40 Ti / TiN bilayers was developed, followed by a TiAlN monolayer and an outer layer of ReN. The selection of the ReN is because this nitride is one of those considered super hard, with hardness around 40 GPa and also has a high chemical and thermal stability. The (Ti/TiN)n/TiAlN/ReN multilayer coatings were co-deposited onto AISI M2 steel by the DC and R.F. magnetron sputtering techniques with a total thickness of 2000 nm. For the deposition of the coatings, Ti, Al and Re targets were used, as well as argon for the deposition of titanium and a mixture of Ar / N2 for the TiN, TiAlN and ReN layers. The SEM images of the cross section revealed a dense and homogeneous columnar growth structure, whose roughness and grain size decreases with the increase in Ti / TiN bilayers, as evidenced by the AFM measurements. The X-ray patterns showed peaks of the fcc cubic phases of ReN, TiAlN and TiN with preferential growth in directions (111) and (110), while only a single peak (110) was observed for Ti with bcc structure. The critical load, determined by the scratch test, increased from 25 N to 40N with the increase in the number of bilayers of the coating. This behavior is associated with the growing compressive residual stresses of the multilayer system as the number of bilayers increases, which was determined by measuring the radius of curvature of selected samples before and after coating them. The hardness of the coatings increased from 22 GPa to 35 GPa and the wear volume decreased substantially with the increase in the period of the Ti / TiN bilayers. The greater resistance to wear is associated with the higher hardness, less roughness and greater adhesion of the coatings as the number of bilayers increases. All deposited coatings showed greater performance in wear tests than uncoated steel.

11:00am **B1-1-ThM-10 High-Power-Density Sputtering of Industrial-Scale Targets: Micromechanical Case Study of Al-Cr-N***, **Fedor F. Klimashin**,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; A. Lümkemann,* PLATIT AG, Switzerland*; J. Kluson, M. Ucik, M. Jilek,* PLATIT a.s., Czechia*; J. Michler, T. Edwards,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

The coatings of cubic (Al,Cr)N are known for their exceptional protective properties, particularly high wear and oxidation resistance. Industrially, these coatings are mainly produced by means of cathodic arc evaporation (CAE). To further improve their performance, elimination of microscopic growth defects (e.g. droplets) is required. One way to achieve this goal could be to utilise a sputtering process. The large dimensions of the targets, however, pose an enormous technological challenge as rather small power (and plasma) densities can be achieved resulting ultimately in underperformance of sputter-deposited coatings.

Here, we introduce a novel sputtering technology allowing to reach high power densities for industrial tube targets. This is realised on the principle of a longitudinal movement of the magnetron inside the target. In doing so, peak power densities of 840 W/cm^2 for the overall power of 25 kW have been achieved. We then produced a series of the novel (Al,Cr)N coatings by sputtering $Al_{60}Cr_{40}$ and $Al_{70}Cr_{30}$ targets (Ø110x510 mm) and compared them to the benchmark CAE (Al,Cr)N coatings. Most of the sputtered coatings have astoichiometric composition, smooth surface and a moderate amount of growth defects. Significant improvements through recipe optimisation could be achieved resulting in hardness (about 35 GPa) and wear rates equal to those of current state-of-the-art CAE coatings. Interestingly, however, micropillar splitting tests revealed a significantly lower fracture toughness (2.5–3 MPa√m) as compared to their CAE counterparts (4–5 MPa√m). Finally, we also compare the results with a series of other industrial ceramic-like coatings, e.g. CrN, (Al,Ti)N, (Al,Ti,Si)N, TiB_2.

11:20am **B1-1-ThM-11 Triboactive CrAlN+XS Coatings Deposited by Pulsed Arc PVD***, K. Bobzin, C. Kalscheuer, **Max Philip Möbius**,* Surface Engineering Institute - RWTH Aachen University, Germany

Arc physical vapour deposition (PVD) is a widely used technology for coating deposition. Besides its advantages regarding deposition rate and the degree of ionization it shows open potential for reduced droplet emission and surface roughness respectively without a decreased deposition rate as with filtered arc PVD. A reduced surface roughness is highly relevant in tribological applications where friction reduction is targeted, especially under dry-running conditions. CrAlN+XS coatings with X = Mo, W show potential for friction and wear reduction under dry-running conditions due to their ability to form the solid lubricants MoS2 and WS2. However, the deposition of electrically low conductive materials like MoS or WS is challenging for arc PVD at the current state of the art. Pulsed arc PVD is a promising technology to reduce droplet emission and surface roughness and additionally vaporize low conductive materials. In this work, CrAlN+XS coatings were developed using pulsed arc PVD. Basic coating and compound properties were analyzed regarding the influence of the incorporation of triboactive elements S, Mo, W. Additionally, a variation of pulse parameters was investigated on CrAlN+MoS coatings. Subsequently, tribological investigations of the CrAlN+XS coatings were performed under dry-running conditions using a pin on disk (PoD) tribometer. Besides wear and friction analysis the tribofilms on the coated basic parts and the uncoated 100Cr6 counter parts were investigated by Raman spectroscopy. Using pulsed arc PVD can decrease the droplet emission and therefore the surface roughness of the coatings. Under dry-running conditions the triboactive coatings show significantly lower wear. Additionally, the coefficient of friction (CoF) can be decreased compared to uncoated steel references. Nevertheless, further coating development is required to decrease the CoF to industrial relevant levels. For the first time CrAlN+XS coatings X = Mo, W were deposited using pulsed arc PVD. The CrAlN+MoS coating shows the highest sulfur content of xS = 9 at.-% verified by electron probe micro analysis (EPMA). Tribofilm analysis provided the proof of concept that CrAlN+MoS coatings deposited by pulsed arc PVD can form the solid lubricant MoS2 under tribological load. This could be consistent with a reduced CoF. The results showed that pulsed arc PVD is a promising technology for applications where the evaporation of electrically low conductive target materials is required for coating deposition and a low surface roughness is targeted.

11:40am **B1-1-ThM-12 Mechanical and Electrochemical Properties of AlCrN/FexN Coating Deposited onto AISI 4140 Steel***, **Omar Ramirez-Reyna**,* National Polytechnic Institute, Mexico*; J. Pérez-Álvarez,* University of Guadalajara, Mexico*; G. Rodríguez-Castro,* National Polytechnic Insitute, Mexico*; C. Rivera-Tello,* University of Guadalajara, Mexico*; A. Meneses-Amador,* National Polytechnic Institute, Mexico

In this study, aluminium chromium nitride (AlCrN) and iron nitrides (Fe_xN) layers were formed on the surface of AISI 4140 steel through the cathodic arc PVD and gas nitriding processes, respectively. Three systems were evaluated by mechanical, adhesion and corrosion tests: AlCrN monolayer coating [AlCrN], duplex coating formed by AlCrN onto an iron nitrides interlayer [AlCrN/Fe_xN] and only nitrided substrate [Fe_xN]. The physicochemical characterization was performed by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and X-ray diffraction (XRD). The AlCrN coatings thicknesses were 2.2 and 3 µm for AlCrN and AlCrN/Fe_xN, respectively; whereas for Fe_xN it was 10 µm. The mechanical properties were obtained by cross-sectional Berkovich indentation tests, where the Fe_xN interlayer in the duplex coating AlCrN/Fe_xN increase the hardness respect the single processes. Moreover, the adhesion of the coatings was evaluated in accordance with the VDI 3198 norm. The AlCrN/Fe_xN coating presented the best adhesion. Finally, the coatings were evaluated by Potentiodynamic Polarization (PD) and Electrochemical Impedance Spectroscopy (EIS), using a conventional three electrode cell. All experiments were performed in a NaCl 3.5% wt. solution at 25 °C. In conclusion, the AlCrN/Fe_xN duplex coating exhibited better behaviour under same testing conditions as compared with the AlCrN and Fe_xN coatings, due to the presence of the iron nitrides interlayer.

12:00pm **B1-1-ThM-13 Mechanical and Electrochemical Properties for SiC_XN_Y Coating as a Function of Nitrogen Content***, L. Chang, **Pin-Feng Huang**, B. Chen, S. Tsai,* Ming Chi University of Technology, Taiwan

Amorphous silicon carbon nitride (a-SiC_xN_y) coatings were prepared on boron-doped silicon and 304 stainless steel substrates by high-power pulsed magnetron sputtering system. Employing the structural and chemical analysis by XRD, XPS(X-ray photoelectron spectroscopy), FE-EPMA(Field Emission-Electron Probe Micro-Analyser) and Raman spectroscopy, it was possible to determine that this coating presents a structure formed by an amorphous zone (a-SiC_xN_y). The a-SiC_xN_y coating with 23.3 at.% N demonstrates a hardness value of 21.7 Gpa. The friction coefficient of the coating with a high C-C bond content against a WC ball is as low as 0.07. The electrochemical behaviors of the deposited coatings in 3.5 wt.% NaCl solution were studied by using potentiodynamic polarization, electrochemical impedance spectroscopy, OM and SEM. The results show that the coated 304 stainless steel displays a better resistance to uniform and pitting corrosion than the bare material.

Keywords: SiC_xN_y, HiPIMS, Electrochemical properties, Amorphous

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