Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B4-2

Properties and Characterization of Hard Coatings and Surfaces

Moderators: Ulrich May, Robert Bosch GmbH, Diesel Systems, Fan-Bean Wu, National United University, Taiwan, Farwah Nahif, eifeler-Vacotec GmbH

1:30pm **B4-2-1 Target Race Track Chemistry is Different to What you Think: XPS Findings from Reactive dc and High Power Impulse Magnetron Sputtering Experiments*, Grzegorz Greczynski,*** Linköping University, IFM, Thin Film Physics Division, Sweden*; S Mráz,* RWTH Aachen University, Germany*; L Hultman,* Linköping University, IFM, Thin Film Physics Division, Sweden*; J Schneider,* RWTH Aachen University, Germany

It is demonstrated, that high power impulse magnetron sputtering (HIPIMS) of Ti target in Ar/N_2 atmosphere results in the formation of a nitride layer in the center portion of the race track, which is much thicker than during conventional dc process. Evidence comes from XPS *ex-situ* analyses of native Ti target surface chemistry [1][2] as well as from complementary sputter depth profiles, which reveal that, under identical process conditions and with N partial pressure optimized to yield stoichiometric TiN films, the compound layer is a factor of 2.5× thicker during HIPIMS. Even at values too low to yield stoichiometric TiN films on the substrate, the ~ 50 Å thick surface region of the HIPIMS operated target is severely nitrided ($N/Ti \gtrsim 0.9$), which is in stark contrast to dc magnetron sputtering where stoichiometric layers can be grown while avoiding target poisoning.[3] TRIDYN simulations of ion/target interactions reveal that such deep N implantation is only possible if N^+ dominates the ion flux to the target during HIPIMS. These results are crucial for an understanding of reactive HIPIMS sputtering processes and finding robust working points necessary to grow high quality functional coatings at acceptable deposition rates.

[1] G. Greczynski, I. Petrov, J.E. Greene, and L. Hultman, *J. Vac. Sci. Technol. A* 33 (2015) 05E101

[2] G. Greczynski, S. Mráz, L. Hultman, and J.M. Schneider, *Appl. Phys. Lett*. 111 (2017) 021604

[3] W. D. Sproul, D. J. Christie, and D. C. Carter, *Thin Solid Films* 491 (2005) 1

1:50pm **B4-2-2 Measurement of Residual Stress on TiN/Ti Bilayer Thin Films using Average X-ray Strain (AXS) Combined with Nanoindentation Methods*, JiaHong Huang,*** *S Lei,* National Tsing Hua University, Taiwan*; H Chen,* National Chiao Tung University, Taiwan

Pure metal interlayers are commonly applied in the hard and protective coatings to relieve residual stress and enhance adhesion on substrate materials. Although extensive studies have been performed in the past two decades, the effect of stress relief by a pure metal interlayer has not been fully understood, mainly due to the difficulty in accurately measuring residual stress in the individual layer of a bilayer coating. Recently we proposed a method combining average X-ray strain (AXS) and the elastic constant determined by nanoindentation (E_{NI}) to accurately measure the residual stress of hard coatings with an uncertainty < 10% [1,2], which provided an effective tool to respectively measure the layer stress in a bilayer coating. Since TiN/Ti is one of the most popular bilayer combinations, TiN/Ti coating was chosen as the model system in this study. The objective of this study was to accurately determine the residual stress in the individual layer of the TiN/Ti bilayer specimens by the newly proposed method. TiN specimens with three different Ti interlayer thicknesses, 50, 100 and 150 nm, were deposited on Si substrate using unbalanced magnetron sputtering. The residual stresses in TiN top layer and Ti interlayer were separately determined by combining AXS and E_{NI}, where AXS was measured using both lab X-ray and synchrotron X-ray sources. The overall stress of the entire TiN/Ti specimen was measured by laser curvature technique. The results showed that the Ti interlayer with thickness larger than 100 nm could relieve residual stress of the bilayer specimen. However, when the interlayer thickness was insufficient (50 nm), the stress of the entire specimen may increase instead of decrease even the interlayer was added. It was found that the Ti interlayer with thickness of 50 nm was subjected to a compressive stress, while interlayers with thickness of 100 nm and above were under a tensile stress. A physical model was developed to describe the stress variation with the interlayer thickness, which could delineate the experimental findings where a switch of stress state from tension to compression occurred in the interlayer at a critical interlayer thickness. In addition, the switch of stress state in the interlayer may be also associated with the stress in the top layer. As the stress in the top layer increases, the interlayer thickness where the transition of stress state occurs will increase.

[1] A.-N. Wang,C.-P. Chuang,G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 262 (2015) 40.

[2] A.-N. Wang, J.-H. Huang, H.-W. Hsiao, G.-P. Yu, Haydn Chen, Surf. Coat. Technol., 280(2015) 43.

2:10pm **B4-2-3 Challenges and Recent Progress in the Development of Arc Evaporated ($(Al_{1-x}Cr_x)_2O_3$) Coatings*, Christian Koller,*** *A Kirnbauer, V Dalbauer, R Raab,* CDL-AOS at TU Wien, Austria*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria **INVITED**

Ceramic Al_2O_3-based coatings have been utilised for technical and functional purpose for decades. Their popularity with respect to protective applicability is based on the excellent combination of mechanical integrity, thermal stability, and chemical resistance. Physical vapor deposition (PVD) belongs to synthesis techniques of choice for industry, as process conditions allow for the utilisation of temperature sensitive substrate materials. Crystalline Al_2O_3 films can be grown at 600 °C and below, but the phase composition is in many cases dominated by metastable Al_2O_3 polymorphs and not the more favourable thermodynamically-stable corundum (α) structure. Among different alloying elements investigated with respected to their ability to stabilise the α-phase, Cr appears to be the most promising candidate. Only recently studies on $(Al_{1-x}Cr_x)_2O_3$ films were extended to cathodic arc evaporation. In order to develop protective coatings with an optimised property spectrum it is imperative to have a comprehensive knowledge of interdependencies of the synthesis procedure. This in first place includes process parameters and structure-property relationships, but it also implies a profound understanding of arc-induced modifications at the cathode surface and the ability to link these to the coating performance. We therefore study on the structural evolution of $Al_{1-x}Cr_x$-based coatings grown in intermetallic state and their transition to stoichiometric oxides, both as a function of the Cr content and oxygen flow rate, and in further consequence examine cathodes and macroparticles with different compositions. Monolithically-grown and gradient-structured (for which the oxygen flow-rate was gradually increased during the synthesis), coatings were prepared by $Al_{0.75}Cr_{0.25}$, $Al_{0.70}Cr_{0.30}$, $Al_{0.50}Cr_{0.50}$, or $Al_{0.25}Cr_{0.75}$ cathodes and investigated with respect to their mechanical properties, thermal stability and oxidation behaviour. By the example of stoichiometric $Al_{0.70}Cr_{0.30}$-based oxides, the impact of alloying elements on either a promotion of the hexagonal corundum structure the stabilisation of transient phases is discussed and the significance of an optimised microstructure is demonstrated by multilayer architectures containing α-structured $(Cr,Al)_2O_3$ seed layers.

By taking different aspects of the cathodic arc evaporation process into account—i.e., cathode surfaces, droplets, oxide phase formation during synthesis—we could provide a further understanding towards the controlled synthesis of $Al_{1-x}Cr_x$-based coatings and thus introduce new concepts for their industrial application.

2:50pm **B4-2-5 Steel Doctor Blade Deposited by HIPIMS-CrN for Protection Purpose*, Jia-Hong Zhou,*** *Y Liou, Y Chen, J He,* Feng Chia University, Taiwan

Doctor blade has long been used for printing, tape casting process, thin sheet formation, etc, where corrosion and wear environments are encountered. Relatively few study work is revealed for improving the performance of the blade edge to resist wear and corrosion attack. In addition to the wet processes having been considered for protection purposes, this study focuses on CrN coating by using high power impulse magnetron sputtering (HIPIMS), which provide dense and strong film adhesion. It is anticipated that with this layer, it would be possible to provide improved corrosion and wear resistance for steel doctor blade. Substrate fixturing technique is developed. The microstructure of the obtained HIPIMS-CrN is examined. Results of field test are compared with the laboratory test for the blading performances.

3:10pm **B4-2-6 In-Line HIPIMS-TiNxOy to Produce Colorful Decorative Coatings*, Yu-De Liou,*** *Y Chen, J He,* Feng Chia University, Taiwan

Many study works based on batch-type PVDs (physical vapor deposition) have been commercialized, as an alternative to wet processes, due to their environment-friendly and color adjustable characteristics, as well as many other features. However, it will be more feasible to use in-line PVD system to produce decorative coatings by taking the advantages of cost-effectiveness, small-piece handling capability and high through-put production.

In the present study, the decorative coatings based on TiNxOy are produced on motorcycle chain plates by using in-line system, where high power impulse magnetron sputtering (HIPIMS) technique is powered. It is found that the obtained coatings are strongly adhered with their color adjustable over a large range (blue, orange, peach red, ocean blue, gem green, champagne gold, violet purple and rosy gold, etc). The color can be controlled by the repeated entering of the tray (substrate holder) into deposition zone as well as the flow ratio of oxygen to argon during deposition. As a whole, the in-line HIPIMS system is feasible for producing high-quality decorative coatings.

3:30pm **B4-2-7 Property of AIP Deposited Thick TiAlN Coating and Application to Actual Steam Turbine for Solid Particle Erosion Protection***,* ***Kenji Yamamoto****, J Munemasa,* Kobe Steel Ltd., Japan*; Y Liang,* National Cheng Kung University, Taiwan*; T Abe,* Toshiba Corporation, Japan*; S Takada, T Takazawa, Y Iwai,* University of Fukui, Japan

Erosion by high velocity solid particle (SPE) can produce a significant damage to high speed-moving aerodynamic objects such as blades for steam turbine or jet engine. SPE can cause a dimensional change and the result is compromising in aerodynamic integrity. Commonly these parts are made of ferrous alloy or light weight Ti alloy and erosion resistance of these metallic materials are not satisfactory. In case of steam turbine blade, mainly magnetite (Fe3O4) particles with relatively large diameter up to 150 um are generated due to the oxidation of inner side of boiler tube and transferred by high velocity steam to the turbine.

High temperature diffusion layer such as boronizing or thermal sprayed metal carbide is commonly used for preventing SPE. But recently, more SPE resistant PVD deposited hard nitride compounds such as TiN[1], TiSiN[2] or TiAlN[3] are in consideration. As the particle diameter becomes larger, it is increasingly difficult to obtain enough SPE resistance with thin coating and at least coating with more than 10um of thickness, preferably more, is necessary. PVD deposited nitride, however, is in large compressive stress and difficult to deposit thick coating particularly on complex shaped parts.

Kobe Steel developed a new magnetically steered cathodic arc source “SFC” which is characterized by a variable control of residual stress of coating. With this new arc source, low-stress and thick TiAlN coatings were deposited and structural and mechanical properties were investigated. TiAlN coatings with different Al compositions were deposited by SFC and erosion resistance was evaluated by MSE method [4] using 50 um alumina particle. It was found that best erosion resistance is obtained at Al composition between around 50 at%. The erosion rate of AIP-TiAlN is more than one order of magnitude smaller compared with conventional surface treatments such as boronizing or CrC thermal spray coating. Thick TiAlN coatings were also applied to fatigue and creep specimens made of 12 mass% Cr steel blade material and effect of coating on fatigue and creep resistance was investigated. The result showed that these properties remained unchanged by TiAlN coating. And finally, the thick TiAlN coating is applied to blades of an operating steam turbine in Japan and now they are in evaluation until the next overhaul.

References:

[1] Feuerstein et al. Surf. Coat. Technol. 204 (2009) 1092

[2] El-Rahman et al. Surf. Coat. Technol. 258 (2014) 320–328

[3] Yamamoto et al. “High-velocity particle impact erosion resistance of PVD deposited hard nitride coatings” presented at ITC 2011, Hiroshima

[4] Y. Iwai et al. Lubrication Science Vol.21, No. 6(2009)213226

3:50pm **B4-2-8 Stress Evolution during Cr_2AlC Film Growth***,* ***Andrius Subacius****, A Matthews,* University of Manchester, UK*; M Hans, S Mráz, J Schneider,* RWTH Aachen University, Germany

Cr_2AlC is a compound which belongs to the family of materials known as MAX phase. The general formula that describes this kind of compound can be expressed as $M_{1+n}AX_n$, where M is a transition metal, A is an A group element, and X is either carbon or nitrogen. MAX phase compounds are regarded as promising for certain applications due to some distinctive characteristics, such as being machinable, having good electrical and thermal conductivity and being resistant to thermal shock.

Residual stress in any film can be a major problem affecting the film properties and limiting the thickness to which they can be grown, due to the risk of debonding. Therefore, it is important not only to evaluate the stress value after the film deposition but it is also beneficial to observe the stress evolution during the growth of the film. In this work, we observed the stress evolution of Cr_2AlC films during their growth. The films were deposited by DC magnetron sputtering from 2 or 4 compound targets at an average power density of 5 W/cm^2 each. Depositions were carried on in argon atmosphere at constant pressure of 3 mTorr (0.4 Pa). Substrate temperature was kept constant at 600 °C. Film thicknesses produced were between 2 mm and more than 8 mm. The in situ stress measurements were performed using a Multi-beam Optical Sensor (MOS) system by monitoring the curvature of the substrate and film with an array of parallel laser beams and a CCD detector. Stress values were calculated using Stoney’s formula.

The residual stress of Cr_2AlC films was compressive ranging from about -1000 MPa to -200 MPa during the single film deposition process. In the early stages of the film growth the compressive stress is dominant reaching a peak value. As the film grows thicker the compressive stress decreases and becomes nearly constant.

4:10pm **B4-2-9 Composition and Temperature Influence on ZrAlN/TiN Multilayer Structure: In-situ X-ray Scattering during Growth, and Transmission Electron Microscopy Studies***,* ***Naureen Ghafoor,*** Linköping Univ., IFM, Thin Film Physics Div., Sweden*; H Wang,* Linköping Univ., IFM, Thin Film Physics Div. and Max-Planck-Institut für Eisenforschung GmbH, Sweden*; J Muhammad, L Rogström, J Schroeder,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; D Ostach, N Schell,* Helmholtz-Zentrum Geesthacht, Germany*; J Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

A massive industrial sector uses hard ware resistance thin films for applications involving extreme temperatures and pressures, and to reform energy and cost-efficiency they constantly call for novel and/or improved materials and coating designs. Over the last 8 years [1-5], we have investigated self-organised ZrAlN nancomposites and related nanolaminated structures for such applications. We have shown that high immiscibility of ZrAlN alloys and sufficient mobility during growth lead to formation of nanostructures which possess high mechanical and thermal stability. The composite formation vary upon varying structural design and composition-temperature window and these parameter-space is a focus in this work.

Here, we present in-situ high-energy synchrotron wide angle X-ray scattering (WAXS) during growth of magnetron sputtered $Zr_{0.75}Al_{0.25}N$/TiN and $Zr_{0.5}Al_{0.5}N$/TiN multilayers complemented with structural characterization using cross-sectional transmission electron microscopy of as-deposited films[6]. The films are grown on MgO (001) substrates in Ar/N2 mixture at substrate temperatures between 350 °C- 950 °C. In situ characterization revealed epitaxial multilayer growth simultaneous to complete segregation of cubic-ZrN and wurtzite-AlN in $Zr_{0.5}Al_{0.5}N$/TiN deposited at 950 °C. When deposited at 350 °C, a preferential 002 texture evolve in these high Al containing films with two phase structure in nanocomposite layer with c- ZrAlN and h-AlN-rich phases. Low Al content in $Zr_{0.75}Al_{0.25}N$/TiN results in single phase c-ZrAlN layers with 111 texture when deposited between 350 °C- 675 °C, and dual phase c-ZrN and w-AlN evolve at 825 °C. The composition-temperature windows for dense smooth films and for the formation of advantageous TiZrN phase at the interfaces are determined. In general, 1D-WAXS obtained in post analysis are consistent with the result of lab-scale XRD and 2D-WAXS patterns resembles SAED patterns for all the $Zr_{1-x}Al_xN$/TiN multilayers studied in this work.

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[2] N. Ghafoor, et al., APL Materials, 1 (2013) 022105-022101--022105-022106.

[3] K. Yalamanchili, et al., Acta Materialia, 89 (2015) 22-31.

[4] L. Rogström, et al., Thin Solid Films, 520 (2012) 6451-6454.

[5] L. Rogström, et. al, Journal of Applied Physics, 118 (2015) 035309.

[6] J.L. Schroeder, et al., Review of Scientific Instruments, 86 (2015) 095113.

4:30pm **B4-2-10 Self-toughening in the TiAlN System***,* ***Matthias Bartosik,*** TU Wien, Institute of Materials Science and Technology, Austria*; C Rumeau, R Hahn,* TU Wien, Austria*; Z Zhang,* Austrian Academy of Sciences, Austria*; P Mayrhofer,* TU Wien, Austria

Titanium aluminum nitride has evolved to one of the most well established hard coating systems over the last decades. Its industrial success is mainly based on the superior oxidation and wear resistance as compared to titanium nitride as well as its age hardening ability. Though Ti-Al-N is among the most widely studied thin film materials, up to now scarcely any attention has been paid to its fracture toughness. Here we report on the evolution of the fracture toughness of Ti-Al-N upon ex-situ vacuum annealing [1]. We found that Ti-Al-N ceramic coatings become harder and tougher simultaneously - two material properties which are often mutually exclusive. The exceptional properties are attributed to the formation of a self-organized nanostructure and precipitation of severely distorted B4 AlN with multiple stacking faults and indications of nano-twins that evolve upon annealing. The fracture toughness was evaluated by performing single cantilever bending tests on free-standing, 2 µm thick, sputtered Ti-Al-N coatings. Additionally, cube corner experiments were conducted on coated Al_2O_3 substrates.

[1] M. Bartosik, C. Rumeau, R. Hahn, Z. Zhang, P.H. Mayrhofer, Fracture toughness and structural evolution in the TiAlN system upon annealing, *under revision*.

4:50pm **B4-2-11 Load Sensing Characterization of Silicon Oxide Coatings***,* ***Tomasz Liskiewicz****,* Leeds University, UK*; I Kolev,* Hauzer Techno Coating, Netherlands*; E McNulty, A Neville,* Leeds University, UK

Due to their high transparency, hardness, flexibility, barrier properties and hydrophilic properties [1,2], silicon oxide (SiO_x) coatings have been employed in a variety of industries including pharmaceutical, food packaging, corrosion protection as well as optical and electronic manufacturing [3,4].

In this work, SiO_x coatings were deposited on stainless steel substrates using the PECVD method with hexamethyldisiloxane (HMDSO) as a silicon precursor and oxygen (O_2) as the process gas. The HMDSO/O_2 ratio was varied between 1:1 and 1:36 in order to create coatings with different stoichiometry, and deposition time was varied to produce coatings with a total thickness ranging from 0.46 to 6.44µm. Coatings were characterised for their scratch resistance, nano-indentation hardness and elastic modulus, chemical composition (EDX) and crystallographic structure (X-Ray diffraction).

A dedicated test setup was developed in this study allowing measurement of coatings' insulating properties under mechanical stresses by simultaneous application of direct voltage through electrodes system, and mechanical compressive stress through varied normal load. The results obtained under constant normal load indicated that SiOx coatings are efficient insulators, characterised by electrical resistivity ranging from 1.62 to 9.72 GΩ-cm, sheet resistance from 15.10 to 38.12 TΩ/square and conductivity from 0.10 to 0.62 (GΩ-cm)-1. Moreover, coatings' insulating properties were characterised under ramped normal load, allowing to tune their load sensing capability by correlating applied mechanical stress with electrical response.

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5:10pm **B4-2-12 The Mechanical and Tribological Properties of TiZrNbN and TiZrNbN-Cu Films***,* ***Ihsan Efeoglu****,* Atatürk University, Turkey*; H Aghdam, A Keles,* Ataturk University, Turkey*; O Baran,* Erzincan University, Turkey*; Y Totik,* Atatürk University, Turkey

">Due to improve friction and wear properties of cutting tools, various films are deposited on high speed tool steel. Transition metal nitride films are common used films for cutting tools. But with the developing technology, transition metal nitride films are inadequate. Therefore, soft metal such as Cu is used to improve the mechanical and tribological properties of transition metal nitrides. So, in this study, TiZrNbN and TiZrNbN-Cu films were deposited under two different working pressure (0.26 Pa and 0.33 Pa) on M2 high speed steel substrate with closed field unbalanced magnetron sputtering (CFUBMS). The microstructure and thickness values were examined with SEM. The chemical composition was determined by EDAX. The crystal phase orientation, grain size and texture coefficient were evaluated by XRD. The mechanical properties and critical load values of the films were obtained by microhardness test and scratch tester, respectively. Tribological properties of films were analyzed with a pin-on-disc tribometer. The hardness values and grain sizes were calculated ranging from 9.5-30 GPa and 17-45 nm, respectively. The atomic contents of Cu were 0.99% and 7.5% at 0.26 and 0.33 Pa working pressures,respectively. The grain size increased with decreasing hardness value and increasing Cu content. The maximum critical load was obtained in the softest film as 75 N. TiZrNbN-Cu films have better mechanical and tribological properties than TiZrNbN films under the same working pressures.

Author Index

Bold page numbers indicate presenter