Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B4

Properties and Characterization of Hard Coatings and Surfaces

B4-1 Investigating the Influence of Nanocomposite Structure on the Thermal Stability of Ag in VSiCN-Ag Coatings*, **Forest Thompson (forest.thompson@sdsmt.edu)**,* South Dakota School of Mines and Technology, USA*; F. Kustas,* NanoCoatings, Inc., USA*; G. Crawford,* South Dakota School of Mines and Technology, USA

Self-lubricating coatings have been studied extensively for elevated temperature tribological applications. For coating designs in which a noble metal solid lubricant phase is continuously supplied to the surface from within a ceramic-based matrix, control of noble metal out-diffusion can be challenging. To investigate the potential of manipulating nanocomposite structure to better control solid lubricant stability and transport, VSiCN and VSiCN-Ag nanocomposite coatings were deposited by plasma-enhanced reactive magnetron sputtering. A nominal Ag content of 4 at.% was maintained while amorphous phase content was varied with the intent of modifying coating density, grain size, and grain morphology. As-deposited coatings were characterized by energy dispersive X-ray spectroscopy, scanning electron microscopy, X-ray diffraction, and transmission electron microscopy. Hardness and apparent elastic modulus were measured by nanoindentation. The thermal stability of Ag within the coatings was evaluated by inspection of the coating surfaces after vacuum annealing at 550°C. Relationships among coating microstructure and Ag thermal stability are identified and potential influences on coating performance in tribological applications are discussed.

B4-2 Spinodal Decomposition of Reactively Sputtered VAlN Thin Films*, **Marcus Hans (hans@mch.rwth-aachen.de)**, H. Rueß,* RWTH Aachen University, Germany*; Z. Czigány,* Centre for Energy Research, Hungary*; J. Krause, P. Ondračka, D. Music, S. Evertz, D. Holzapfel,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J. Schneider,* RWTH Aachen University, Germany

We investigate the decomposition mechanisms of metastable cubic (c–)$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ thin films, grown by reactive high power pulsed magnetron sputtering, by combination of structural and compositional characterization at the nanometer scale with density functional theory (DFT) calculations. Based on thermodynamic considerations of $d^2G/dx^2 < 0$, spinodal decomposition is expected for c-$V_{1-x}Al_xN$ with $x \geq 0.35$. While no indications for spinodal decomposition are observable from laboratory and synchroton diffraction data after annealing at 1300°C, the formation of wurtzite (w–)AlN is evident after annealing at 900°C by utilizing high energy synchrotron X-ray diffraction. However, the complementary nature of elemental V and Al maps, obtained by energy dispersive X-ray spectroscopy in scanning transmission electron microscopy mode, imply spinodal decomposition of c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ into V- and Al-rich cubic nitride phases after annealing at 900°C. These chemical modulations are quantified by atom probe tomography and maximum variations of x in $V_{1-x}Al_xN$ are in the range of 0.36 to 0.50. The magnitude of the compositional modulations is enhanced after annealing at 1100°C as x varies on average between 0.30 and 0.61, while the modulation wavelength remains unchanged at approximately 8 nm. Based on DFT data, the local x variation from 0.30 to 0.61 would cause lattice parameter variations from 4.111 to 4.099 Å. This difference corresponds to a shift of the (200) peak from 44.0 to 44.1°. As the maximum decomposition-induced peak separation magnitude of 0.1° is significantly smaller than the measured full width at half maximum of 0.4°, spinodal decomposition cannot be unravelled by diffraction data. However, consistent with DFT predictions, spinodal decomposition in c–$(V_{0.64}Al_{0.36})_{0.49}N_{0.51}$ is revealed by chemical composition characterization at the nanometer scale.

B4-3 Effect of Functionally Graded Layers on Tribological Behavior of TiZrN Coatings on AISI D2 Steel*, **Jia-Hong Huang (jhhuang@ess.nthu.edu.tw)**, B. Tsai,* National Tsing Hua University, Taiwan

The objectives of this study were to investigate the role of TiN transitional layer and Ti interlayer in the tribological behavior of tri-layer TiZrN/TiN/Ti coatings and to explore the mechanism of stress relief in the tri-layer coatings. TiZrN coatings were deposited on AISI D2 steel by DC unbalanced magnetron sputtering. There were three series of samples, including single layer TiZrN (S), bilayer TiZN/Ti (B), and tri-layer TiZrN/TiN/Ti (Tx) in this study. The TiN thickness of Tx-series specimens ranged from 200 to 400 nm. The N/(Ti+Zr) ratios of TiZrN layer ranged from 0.9 to 1.0 and the Zr/(Zr+Ti) ratio of TiZrN coatings was about 0.5. The hardness of the specimens varied from 28.1 to 31.9 GPa which slightly decreased by introducing TiN transitional layer. The residual stress of TiZrN layer decreased from -8.56 to -3.28 GPa with increasing thickness of interlayer and transitional layer. Scratch test was used to evaluate adhesion strength. The results showed high L_{c2} critical loads for all specimens ranging from 63.2 to 88.6 N. The TiN transitional layer could improve the adhesion strength, and the L_{c2} increased as the thickness of transitional layer increased. The wear rate of the tri-layer coatings was lower than that of TiZrN single layer and bilayer coatings. The results indicated that introducing the interlayer and transitional layer could enhance the wear resistance. The wear rate almost linearly increased with increasing elastic stored energy (G_s) that was related to elastic constants, residual stress and coating thickness [1]. The difference between the fracture toughness (G_c) and G_s can be considered as the capability that the coating can absorb externally input energy. The increase of Gs may decrease the capacity in absorbing energy and thereby decreasing the wear resistance. Therefore, G_s could be taken as an index to evaluate the wear resistance of coatings [2].

Reference

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[2] Yu-Wei Lin et al., Surf. Coat. Technol. 350(2018)745.

B4-4 Thin Film Characterization by Picosecond Ultrasonics on High Curvature Surfaces*, **Frederic Faese (ffaese@neta-tech.com)**, J. Michelon, X. Tridon,* Neta, France

Since the discovery of picosecond ultrasonics by H. J. Maris and his team in 1984, this nondestructive technique continuously expanded and found numerous applications. Where the first application concerned thin film thickness measurement in the semiconductor industries with a complex setup, picosecond ultrasonics technique is now much more efficient, user-friendly and widespread. Indeed, thickness measurement is now easily reachable and this technique also allows the elastic properties measurement of thin films, multilayers and nanostructures, adhesion properties evaluation, etc. Thus, among all the fields that are potentially interested in this new technique are mainly surface engineering, microelectronics and biology.

We will see how the photo-generation and the photo-detection of ultra-high frequency ultrasounds (of the order of THz) can accurately and rapidly measure the thickness of a TiN hard coating on a Ti substrate. This measurement can be performed either locally with a high spatial resolution or by scanning the sample, hence giving a mapping of the thickness measurement on the whole surface. Up to now, the shape of the samples had to be very flat; in this presentation, we will demonstrate that we can also analyze even highly curved samples. Compared to concurrent techniques such as ellipsometry or the Calo tester, picosecond ultrasonics presents the unique advantages to be contactless, nondestructive and able to evaluate the properties of a complex shape sample. To illustrate this last point, results will be presented showing outstanding features such as an advanced 3D mapping of a hard coating thickness on a cylinder or a sphere.

B4-5 Fatigue Behaviour of Thin Coating and the Influences of Plastic Deformation of Harden-case using Irreversible Cohesive Zone Model*, **Jiling Feng (j.feng@mmu.ac.uk)**,* Manchester Metropolitan University, UK*; Y. Qin,* University of Strathclyde, UK*; T. Liskiewicz,* Manchester Metropolitan University, UK*; B. Beake,* Micro Materials Ltd, UK

Cohesive-zone modelling technique has been proved to be an efficient approach to simulate the fracture behaviour of multi-layered coatings under monotonically loading (Feng, 2012). This paper aims to investigate the fatigue failure mechanism of coating system by observing the procedure of initiation and propagation of cracks within the coating under the cyclic loads.

We developed a "three-layer" finite element model, composed of the coating, hardened case and substrate, which was validated via nano-indentation technique with 300 µm radius indenter. Homogenous material properties were assumed for both the TiN/CrN coating and the substrate, with multi-linear hardening behaviour. Prior to coating deposition, the substrate was heat-treated by plasma nitriding to enhance the load-bearing capacity of the coating/substrate system.

An irreversible cohesive constitutive equation, taking into account the energy dissipation resulted from frictional interaction of asperities along the cohesive surfaces and crystallographic slip, was employed to identify the crack initiation and to simulate the crack propagation under the cyclic loads. An in-house User Material (UMAT) subroutine was used to simulate the degradation of coating material upon cyclic loading.

Numerical results demonstrated a clear quantitative relationship between the coating stiffness degradation and its damage accumulation. It was observed from a case study that first crack (0.01 µm in width and 0.05 µm in depth) was initiated at 8th loading cycle, and it propagated through the coating thickness with increasing number of loading cycles reaching 1.4 µm at the 100th cycle. It was also noticed that the plastic deformation of the hardened case developed significantly, which might be a major contribution of the initiation of the crack.

The results observed in this study are in agreement with our recent experimental observations (Beake et al, 2019), which indicated that micro crack/wear damage was occurring at the early stage of nano-indentation loading cycles. The numerical study confirmed, that once crack was initiated, it propagated rapidly through the coating, which can lead to delamination when the crack reaches the hardened substrate interface.

Key words: Fatigue failure; Cohesive Zone Model; Cyclic loading;

Reference

1. Feng, J & Qin, Y (2012), Prediction of the critical load of a metal-rolling system by considering the damage of the coated surface, Steel Research International, Metalforming, Special Edition.
2. Beake, B.D., Isernm L., Endrino, J.L., Fox-Rabinovich, G.S., (2019), Micro-impact testing of AlTiN and TiAlCrN coatings, Wear, 418–419, 102-110.

B4-6 Microstructure and Oxidation Behaviour of Arc Evaporated TiSiN Coatings Investigated by *in-situ* Synchrotron X-ray Diffraction*, Yvonne Moritz (yvonne.moritz@unileoben.ac.at), C. Saringer, M. Tkadletz,* Montanuniversität Leoben, Austria*; A. Stark, N. Schell,* Helmholtz-Zentrum Geesthacht, Germany*; M. Pohler,* CERATIZIT Austria GmbH, Austria*; N. Schalk,* Montanuniversität Leoben, Austria

TiSiN hard coatings are a suitable candidate as a protective layer for various cutting applications, due to their advantageous mechanical properties and excellent oxidation resistance. Within this work, a detailed characterization of the microstructure of TiSiN is complemented by the investigation of its oxidation mechanism using *in-situ* X-ray diffraction (XRD) at a synchrotron radiation facility. XRD, X-ray photoelectron spectroscopy and transmission electron microscopy investigations of an as-deposited TiSiN coating grown on cemented carbide substrate indicate the presence of a nanocomposite structure, consisting of Ti(Si)N nanocrystallites embedded in an amorphous Si_3N_4 matrix. To illuminate the oxidation stability, a powdered coating was annealed in air between 100 and 1200 °C and the recorded 2D X-ray diffractograms were correlated with the results of differential scanning calorimetry. Sequential Rietveld refinement of the obtained synchrotron data provided temperature-dependent information about the phase composition and thermal expansion of the individual phases. The results revealed an oxidation stability of TiSiN up to a temperature of approximately 830 °C, followed by the formation of both, rutile and anatase TiO_2. It was shown that the quantity of the metastable anatase phase reached its maximum at a temperature of 1020 °C and then continuously transformed into the stable rutile modification at higher temperatures. The present findings provide a detailed insight into the complex microstructure and oxidation mechanism of TiSiN coatings, allowing to further optimize this system for future applications.

Keywords: TiSiN hard coatings, arc evaporated, Sequential Rietveld refinement, oxidation resistance, TEM

B4-7 High Temperature Tribology of Hf Doped c-$Al_{0.67}Ti_{0.33}N$ Cathodic Arc PVD Coatings Deposited on M2 Tool Steel*, G. Mondragón Rodríguez, Alvaro Enrique Gómez Ovalle (a.gomez@posgrado.cidesi.edu.mx), J. Alvarado Orozco, J. González Carmona, C. Ortega Portilla, J. Hernández Mendoza,* CIDESI, Mexico

c-$Al_{(1-x)}Ti_xN$ hard coatings are widely applied due to their thermal stability up to 800 °C, high resistance to wear and oxidation. Due to these characteristics they are frequently deposited on cutting tools used for machining processes. Improvements on the mechanical and oxidation properties are derived from the microstructure characterized by a stable solid solution of Al in TiN. In the present research, undoped a) c-$Al_{0.67}Ti_{0.33}N$ and hafnium doped b) c-$Al_{0.67}Ti_{0.33}Hf_xN$, which were deposited using the cathodic arc technique using 500 sccm of high purity N_2, Temperature = 430 °C, Pressure = 8 x 10-2 mbar, deposition time = 400 Ah, cathode current = 150 A and bias voltage = -80 V. The elemental chemical analysis displays hafnium contents ranging from 1.0 to 2.26 wt. %. The scanning electron microscopy analysis of the surface of both coatings showed similar droplets sizes and defects density produced by the cathodic arc deposition. Through the grazing incidence X-ray diffraction (DRX), the characteristic peaks of a cubic $Al_{1-x}Tix$ N coating were observed for both the reference coating and the doped nitride. Tribology tests of the c-$Al_{0.67}Ti_{0.33}Hf_xN$ coating in an argon jet for 250, 500, 1000, 2500 & 5000 cycles at a temperature of 900 °C showed the evolution and wear behavior under these conditions. The predominant friction mechanisms observed were related to abrasion, showing that hard particle formation and plowing increased wear with increasing distance. Oxidation prevents from further debris formation, while at room temperature debris are oxidized due to friction. The friction coefficients were maintained after the inclusion of hafnium as a doping material, however high temperature wear was reduced. These observations correlated well with the transition and stable oxide phases being formed at 900 °C during the tribology tests.

Keywords: Hf doped, tribology, high temperature tribology, arc PVD.

B4-8 Cross-sectional X-ray Nanodiffraction Characterization of Radiation Damage, Stresses, and Microstructure in Tungsten Coatings*, Kostiantyn Hlushko (kostiantyn.hlushko@unileoben.ac.at),* Montanuniversität Leoben, Austria*; A. Mackova,* Nuclear Physics Institute of the Czech Academy of Sciences*; J. Todt,* Erich Schmid Institute for Material Science, Austrian Academy of Sciences, Austria*; R. Daniel,* Christian Doppler Laboratory for Advanced Synthesis of Novel Multifunctional Coatings at the Department of Materials Science, Montanuniversität Leoben, Leoben, Austria*; J. Keckes,* Montanuniversität Leoben, Austria

A better understanding of depth-dependent radiation damage in protective coatings which can be used in fusion/fission reactors and in space is essential pending step for further development of novel coating types and microstructures that are capable of withstanding severe environments over long time periods. Tungsten is a perspective material for plasma-facing components of a fusion reactor due to its high radiation resistivity, high thermal conductivity and high melting point. In this contribution, 8µm thick nanocrystalline tungsten coating on WC substrate with columnar microstructure was irradiated using Si^{2+} ions with an energy of 5MeV with a fluence of $2x10^{16}$ ions/cm^2.In order to investigate depth-dependent changes in residual stresses and microstructure induced by the irradiation, cross-sectional X-ray Nanodiffraction (CSnanoXRD) with a beam size of 100 nm was applied at European Synchrotron Radiation Facility in Grenoble, France, to scan 50µm samples at the film cross-section. The experimental results revealed significant changes in the depth-dependent gradients of residual stresses as well as with the changes in unstressed lattice parameters, which will be presented together with the data from transmission electron microscopy.

B4-9 Combinatorial Approach for the Synthesis of Thermally Stable High Si-containing Nanocomposite AlCrSiN Coatings*, Michal Zítek (michal.zitek@unileoben.ac.at), N. Jäger, M. Meindlhumer,* Montanuniversität Leoben, Austria*; F. Nahif,* voestalpine eifeler-Vacotec GmbH, Düsseldorf, Germany*; C. Mitterer, R. Daniel,* Montanuniversität Leoben, Austria

High-performance cutting tools are subjected at high cutting speeds to high loads and temperatures typically exceeding 1000 °C. AlCrN alloyed with Si has been shown to be a perspective coating system for protection of cutting tools operating in such harsh industrial environments as it exhibits promising mechanical properties and thermal stability. Especially low Si-containing AlCrN coatings are known for their enhanced mechanical properties as well as improved thermal stability and oxidation resistance due to their nanocomposite structure.

Unlike Si concentrations far below 10 at.% Si, which are frequently reported in literature, the focus of this work is to systematically study arc-evaporated AlCrSiN coatings with a high Si content of about 15 at.%, varying the Al/Cr ratio from 50/50 to 90/10. Elemental composition was controlled by co-evaporation of $(Al_{50}Cr_{50})_{75}Si_{25}$, $(Al_{70}Cr_{30})_{75}Si_{25}$ and $(Al_{90}Cr_{10})_{75}Si_{25}$ cathodes in an industrial-sized deposition system (alpha400P, voestalpine eifeler Vacotec GmbH). This combinatorial approach allowed for a synthesis of coatings with a wide range of elemental composition from $Al_{19}Cr_{21}Si_{16}N_{44}$ to $Al_{30}Cr_5Si_{16}N_{50}$.

XRD measurements revealed that the AlCrSiN coatings display a nanocomposite structure consisting of a mixture of cub-CrN and hex-AlN phases. The observed gradual increase of the Al/Cr ratio led to an increasing compressive residual stress and fraction of softer hex-AlN phase. These two competing mechanisms resulted in hardness of about 25 GPa irrespective of the coating composition, which was preserved even after annealing at 1000 °C in vacuum. That makes this coating system interesting for various high-temperature applications. The thermal stability and oxidation resistance were furthermore studied in detail by differential scanning calorimetry and thermogravimetric analysis in inert atmosphere and in synthetic air to enlighten the origin of the mechanical and structural stability at elevated temperatures. The results show that especially high Si-containing AlCrSiN coatings with Al/Cr ratios higher than 80/20 exhibit excellent oxidation resistance with negligible mass gain up to 1250 °C.

The combinatorial approaches used within this study are powerful in seeking perspective coatings with specific elemental and phase compositions and can be effectively applied also in industrial-sized deposition systems. Moreover, they enable to understand various mechanisms responsible for high thermal stability and oxidation resistance of coatings while combined with modern characterization methods.

B4-10 In-plane Texturing of Silver Thin Films*, **Francesca Corbella (corbella.francesca@gmail.com)**,* Saint-Gobain Recherche/CNRS, France

Pollution and energy waste are main concerns for today's society. In buildings, part of the waste is due to thermal radiation losses through windows1. To address the problem, low-emissive coatings were introduced in the market. By being reflective in the far IR range and transmissive in the visible light, the low-emissive coatings are designed to reduce the heat losses from inside the building to the outside, while maximizing the solar gain. Such properties are achieved through silver based multilayers, deposited on the glass through a PVD process. The efficiency of the coatings is then related to the maximization of the IR reflectance, which depends on the electrical conduction of the nanometric silver layer.2 The minimization of the Ag resistivity becomes, therefore, a key point for enhancing the optical properties of the coatings. In thin films, the conductivity of a material depends on its structural properties, which are influenced by its seed layer. Till today, ZnO was recognized as the best underlayer for Ag and the most used oxide in the industrial glazing. In particular, it was observed that the deposition of the oxide in its textured hexagonal lattice led to the growth of a Ag (111) out-of-plane textured film, with enhanced electrical properties. Film texturization can play an important role on silver conductivity.4-5 Starting from a model ZnO single crystal based stack, our study showed the impact of in-plane and out-plane texturization on silver resistivity . The system was then optimized with the introduction of a buffer polycrystalline ZnO layer, showing promising results. The ultimate goal is to reproduce the structural and electrical properties, observed on the single crystal stacks, in polycrystalline sputtered coatings through Ion Beam Assisted Deposition, a sputtering technique becoming more and more suitable for an industrial implementation.

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B4-12 INVITED TALK: Modern Analytical Methods for Characterizing the Tribological Material Properties of Coatings*, **Dietmar Schorr (dietmar.schorr@dhbw-karlsruhe.de)**,* Cooperate State University in Karlsruhe, Germany **INVITED**

This paper presents photothermal principle as a new method for determining the tribological properties of hard coatings. The coating properties, which determine the friction and wear behaviour of a tribological system, are the coating thickness, the adhesive strength and the hardness. The known classical analysis methods have disadvantages in determining the respective coating properties and are not applicable for many coatings and surfaces. Furthermore, these methods only provide information on the individual coating properties, but not on the overall tribological behaviour of a coating. With the photothermal method, these limits are exceeded and it also works where classical methods fail. Photothermics works non-destructively and can be used to determine the coating properties over a wide area. The photothermal technology works with thick and thin layers, for cohesive and adhesive adhesion testing and is independent of surface roughness.

In photothermal peripheral zone analysis, an intensity-modulated laser spot hits an object surface. The radiation is absorbed on the surface and generates a heat flux that propagates into the interior of the component in the form of thermal waves. The waves have the same frequency as the irradiated laser light. The further propagation of the thermal waves is influenced by the thermal properties of the coating (thermal diffusivity). These cause the waves to be reflected back and radiated at the surface as heat. The thermal resistance of the material ensures that the thermal waves travel through the material with a time delay and that the phase of the radiated heat is offset from the radiated laser. If the thermal properties of the coating change due to thickness, hardness or adhesion strength, this is measured by the phase shift. This is also almost independent of the surface roughness.

The reflected waves are registered by an infrared detector, which is cooled down to increase sensitivity. The penetration depth of the oscillating thermal waves into the interior of the material is determined by the modulation frequency of the laser and depends on the thermal properties of the material. High frequencies in the kHz range are used for layer analysis and low frequencies in the Hz range for material analysis.

B4-14 INVITED TALK: Metal Oxynitride Thin Films: A Review on Synthesis Developments, Performance, and Applications*, **Sharafat Ali (sharafat.ali@lnu.se)**,* Linnaeus University, Sweden **INVITED**

This talk will provide an overview of the latest research development on metal containing nitrogen rich oxynitride thin films as hard, durable and strong material. I will start giving an overview of silicon oxynitride thin, preparation of these films by different techniques and variation of properties with the N content. I will also talk about the new amorphous thin films in the metal containing -Si-O-N systems containing a high amount of nitrogen and metals. Recently we have deposited novel AE-Si-O-N thin-film materials (AE= alkaline earth e.g. Mg, Ca, and Ba), onto float glass surfaces, by magnetron sputtering. Mechanical and physical properties show hardness values up to 22 GPa, reduced elastic modulus values up to 175 GPa and refractive index values up to 2, which can be compared to the uncoated float glass having hardness of 7 GPa, elastic modulus of 65 GPa and refractive index of 1.50. These thin films can be potentially used as a protective cover for displays and touch screens in tablets, smartphones, watches, etc.

B4-16 Influence of the Period of the Substrate Oscillation on Thin CrN Films Obtained by RF Physical Vapor Dynamic Glancing Angle Deposition Technique*, M. Jimenez, F. Cemin, A. Riul, L. Zagonel,* UNICAMP, Brazil*; C. Figueroa,* Universidade de Caxias do Sul, Brazil*; D. Wisnivesky,* UNICAMP, Brazil*; **Fernando Alvarez (alvarez@ifi.unicamp.br)**,* Instituo de Física-UNICAMP, Brazil

The control of the physical properties of hard metallic nitride coatings is mandatory to obtain good performance in applications such as cutting tools. In this work, nanostructured chromium nitride (CrN) films are obtained by combining radio frequency magnetron sputtering (RFMS) and dynamic glancing angle deposition (DGLAD) using Programmable Logic Controller (PLC). By appropriate choosing the substrate oscillation frequency, the physical properties such as micro and nanostructure, morphology, hardness, texture, and crystallite size are feasible to be tailored. Samples are deposited by moving the substrates forward and backward ($-\phi_0 < \phi(t) < +\phi_0$) by controlling the angular velocity $\omega = d\phi/dt$, inducing the formation of wavy-like periodic columnar nanostructures. Herein, we explore the effects prompted by the substrate oscillations at relatively short periods (1 <T< 10 min) on the CrN structure, as well as its influence on some physical and mechanical properties of the columnar films. It is observed the formation of wavy-like nanostructures, that generate the apparent formation of multilayer films. The dependence of the incident flux of particles with the angular position $\phi(t)$ of the substrate and the scattering of the sputtered particles on the gas phase prompt a complex distribution of precursors on the substrate surface. To take in account these effects, the process was simulated by the SiMTra software. Specific details of the results are reported in the Supplementary Information.

Keywords: Hard coatings, Chromium nitride, Dynamic glancing angle deposition, Numerical simulation

B4-17 Fabrication and Microstructure Evolution of Sputtering Single Element Transition Metal Nitride Multilayers*, K. Liu, Y. Yang, J. Xiang, Z. Lin, **Fan-Bean Wu (fbwu@nuu.edu.tw)**,* National United University, Taiwan

Transition metal nitride, TMN, layers nowadays is frequently applied for the enhancement in surface protection applications. Amongst versatile TMN films, multilayer systems attracted intense attentions due to its structure feature and specific strengthening mechanisms. In this work, TaN and MoN single transition metal nitride multilayer coatings were deposited through vacuum sputtering process. Layered configuration was identified since distinct crystal structures, like columnar crystalline, nanocrystalline, and even amorphous features, were manipulated for building layers. The film growth mechanism was discussed in terms of deposition parameters, including gas mixture and sputtering power density. The distinguishable interfaces in the multilayers could be established by different microstructure of adjacent layers. The higher power and larger N_2 gas inlet during deposition generated amorphous layers and suppressed the continuous growth of columnar crystals in crystalline layers. In addition, the high power impulse method was also employed to modify the interfaces between building layers. The intact and flattened interfaces were beneficial to the discontinuity of the microstructure of the building layers for the single transition metal nitride multilayer coatings.

B4-18 Numerical Evaluation of the Contact Fatigue Resistance of AlCrN, N and AlCrN/N Coatings on AISI 4140 Steel*, Andre Ballesteros-Arguello (aballesteros_90@hotmail.com)*, *F. Ramírez-Reyna, A. Meneses-Amador, G. Rodríguez-Castro, D. Fernández-Valdés, O. Reyes-Carcaño,* National Polytechnic Institute, Mexico

An experimental-numerical study of the contact fatigue resistance of coatings over an AISI 4140 steel was developed. Three experimental conditions were carried out: a coating of aluminum chrome nitrides (AlCrN) by physical vapor deposition process (PVD), a coating of iron nitrides (N) by gas nitriding process and finally a multilayer system of AlCrN/N. Contact fatigue tests were performed on a MTS Acumen electrodynamic test system in charge controlled mode, by cyclic loading of a sphere on a flat surface formed by the layer-substrate system. The contact fatigue test methodology consisted of two main stages. First, critical loads were determined under monotonic loads, for each of the systems, where circumferential cracks were considered as the failure criterion. Second, fatigue conditions were performed in a low cycle using subcritical monotonic loads with a frequency of 5 Hz. A numerical model based on the finite element method was developed to evaluate the stress field generated in the systems by cyclic contact loads. The results exhibit a better resistance to contact fatigue in the AlCrN/N multilayer system, due to the presence of the intermediate layer of iron nitrides.

B4-19 Low Temperature Deposition of TiB-based Hard Coating Films by Pulsed DC Plasma CVD*, Takeyasu Saito (tsaito@chemeng.osakafu-u.ac.jp)*, *H. Matsushima, K. Fuji, D. Kiyokawa, N. Okamoto,* Osaka Prefecture University, Japan

Cemented carbide is often used for molds and cutting tools based on high hardness (1800 Hv for WC, 1200-1500 Hv for WC-Co) and toughness (4-6 Mpa・$m^{1/2}$ for WC, 13-20 Mpa・$m^{1/2}$ for WC-Co), in which Ti-based hard coating films are generally used to improve functions such as hardness, heat resistance, durability, releasability and lubricity. Typical Ti-based hard films are TiC, TiN and TiCN, in which TiCN has advantages of TiC with high hardness (3000-3800 Hv) and low friction coefficient (0.1) and TiN with excellent oxidation resistance (ca. 600ºC). In addition, TiB_2 has excellent heat resistance, oxidation resistance (over 400ºC), and high hardness (20-70 GPa). However, it is difficult to form TiB_2 thin film with high growth rate and good crystallinity at low temperatures. It is important to deposit TiB_2 coating films with good crystallinity to get enough hardness, by controlling the ratio of Boron, Carbon and Nitrogen, to balance the superior characteristics of TiB_2 and TiCN.

Physical Vapor Deposition (PVD) or Chemical Vapor Deposition (CVD) are mainly used for Ti-based hard coating films. PVD has the advantage of simple and low-temperature growth (up to 550ºC), on the other hand, thermal CVD (ca. 1000ºC) has a limitation of the base material because of high temperature treatment, whereas adhesion strength and uniformity are superior . Therefore, a film deposition method having good adhesion strength and uniformity at low temperatures is required.

In this study, we focused on lowering the film deposition temperature to increase applicable base material. Growth rate, crystallographic structure, film composition and hardness were measured by a surface profiler, X-Ray Diffraction (XRD), X-Ray Photoelectron Spectroscopy (XPS) and a micro-hardness tester, respectively. We carried out Ti-based or TiB-based hard films synthesis from $TiCl_4$, BBr_3, CH_4, and N_2 using RF plasma CVD, DC plasma CVD, and the pulsed DC plasma CVD. For the case of TiB-based hard coating films by RF plasma CVD, growth rate as 350-800 nm/h was obtained, however, XRD exhibited amorphous or microcrystalline. The hardness was lower than the reported value, possibly due to the amorphous phase and existence of oxygen. For the case of TiC hard coating films by DC plasma CVD, growth rate was up to 800 nm/h, also exhibited amorphous or microcrystalline. Pulsed DC plasma CVD can be expected to crystallize the TiB-based hard film, because by introducing pulse, it is possible to control the electron temperature in the plasma, and to control the dissociation reaction in the plasma and the accumulation of charges on the substrate surface.

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