Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-3-WeM

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

8:20am **B4-3-WeM-2 Physical Properties of Nano-structured Chromium Nitride Hard Coatings obtained by RF Physical Vapor Dynamic Glancing Angle Deposition***, M Jimenez, V Antunes, S Cucatti, A Riul, L Zagonel,* UNICAMP, Brazil*; C Figueroa,* Universidade de Caxias do Sul, Brazil*; D Wisnivesky,* UNICAMP, Brazil*; **Fernando Alvarez,*** Instituto de Física, UNICAMP, Brazil

Nanostructures CrN films are obtained by combining *RF Physical Vapor Dynamic Glancing Angle Deposition* (PV-DGAD) and Logic Programmable Computer (PLC) controlled substrate motion. By appropriated substrate oscillation frequency, the physical properties such as the micro-nanostructure, morphology, hardness, texture, crystallite size are feasible to be tailored. Samples are deposited by moving the substrate forward (-ϕ=> +ϕ) a back (+ϕ => -ϕ) by controlling the angular velocity ω=dϕ/dt. The angle ϕ is measured perpendicular to the substrate (ϕ=0, Cr target parallel to the substrate). We report the physical properties of samples obtained by moving the substrate with ω(t) constant and square shape functions. The time dependence angle of the precursors atoms impinging the substrate prompts the formation of wavy-like and zigzag periodic nano-crystalline columnar nano-structures with interesting physical properties. The physical characteristics of the CrN coating such as morphology, residual stress, nano-hardness, crystallite size and texture of the columnar multi-structured films are customized by the PLC motion of the substrate. Also, X-ray spectra show that the oscillation of the substrate allows the appearance of a periodic crystalline orientations that strongly depends on ω(t). Finally, these properties of the deposition technique open the possibility to control the (un)isotropy of the hard coatings for specific applications.

Keywords: Hard Coating, Chromium nitride, Dynamic Glancing angle deposition

8:40am **B4-3-WeM-3 Synthesis and Characterization of Sputter Deposited Hard Coatings within the Quasibinary System TiB_2–VB_2***, **Christian Mitterer,** V Terziyska, M Tkadletz, L Hatzenbichler, D Holec,* Montanuniversität Leoben, Austria*; V Moraes,* Institute of Materials Science and Technology, TU Wien, Austria*; A Lümkemann,* PLATIT AG Advanced Coating Systems, Switzerland*; M Morstein,* Hightech Zentrum Aargau AG, Switzerland*; P Polcik,* Plansee Composite Materials GmbH, Germany

TiB_2 coatings on cutting tools have become state-of-the-art in high-performance machining of nonferrous alloys, due to their superior hardness, thermal stability and low adhesion tendency to workpiece material. These properties stem from strong covalent B-B bonds within the hexagonal TiB_2 lattice, which consequently results in high brittleness limiting their application. Thus, in this work, coatings within the quasibinary system TiB_2–VB_2 have been investigated, with the goal to tune their chemical bonds to overcome these limitations. Coatings with thicknesses of 2 ± 0.5 µm have been synthesized by d.c. magnetron sputter deposition from powder metallurgically produced $(Ti,V)B_2$ composite targets with 2-inch-diameter and VB_2 fractions of 0, 7, 13, 25, and 100 mol%. All coatings are characterized by a strongly (001) oriented hexagonal AlB_2-type $(Ti,V)B_2$ solid solution phase with a Vegards-like gradual shift of X-ray diffraction peaks from TiB_2 to VB_2. While the compressive stress within the TiB_2 coatings reaches a maximum of -1.4 GPa, VB_2 addition results in stress relaxation to about -0.3 GPa, independent of the VB_2 content. Despite this low stress of $(Ti,V)B_2$ coatings, their hardness and elastic modulus is largely unaffected by the VB_2 addition, reaching values of about 45 GPa and 420 GPa, respectively. In addition, $(Ti,V)B_2$ coatings sputter deposited from targets with 25 mol% VB_2 show superior friction and wear properties during ball-on-disk testing against Al_2O_3 at room temperature and at 400°C, outperforming pure TiB_2 coatings. Finally, the results obtained are corroborated by ab-initio calculations of elastic properties within the TiB_2–VB_2 quasibinary system.

9:00am **B4-3-WeM-4 Deposition-controlled Stabilization of Metastable fcc-(Al,Ti)N in CVD and PVD Coatings***, **Ulrike Ratayski,*** Technische Universität Bergakademie Freiberg, Germany*; M Höhn,* Fraunhofer IKTS, Germany*; B Scheffel,* Fraunhofer FEP, Germany*; F Fietzke,* Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Germany*; M Motylenko, D Rafaja,* Technische Universität Bergakademie Freiberg, Germany

The addition of aluminum nitride to titanium nitride is known to improve the high-temperature oxidation resistance of TiN-based coatings. Furthermore, low or medium concentrations of Al increase also the hardness of the (Ti,Al)N coatings [1]. High Al contents lead typically to an enhanced decomposition of titanium aluminum nitride into Ti-rich (Ti,Al)N with the face centered cubic (fcc) structure and wurtzitic AlN, and to the degradation of the mechanical properties of the Al-rich (Al,Ti)N coatings. In order to be able to achieve good high-temperature oxidation resistance and high hardness concurrently, metastable Al-rich fcc-(Al,Ti)N must be stabilized.

In this comparative study, the mechanisms stabilizing metastable Al-rich fcc-(Al,Ti)N are discussed and tested on the Al-rich (Al,Ti)N coatings containing more than 50 mol % AlN, which were deposited using chemical vapor deposition (CVD), spotless arc evaporation (SAD) and pulsed magnetron sputtering (PMS). The mechanisms stabilizing the thermodynamically metastable phases were concluded from the microstructure analyses that were performed using X-ray diffraction, transmission electron microscopy with high resolution, X-ray spectroscopy (EDX) and electron-energy loss spectroscopy (EELS).

In the (Al,Ti)N coatings prepared by CVD, three-phase composites consisting of fcc-(Ti,Al)N, fcc-(Al,Ti)N and w-AlN have formed. Although w-AlN is known to deteriorate the mechanical properties of the (Al,Ti)N coatings, the interaction of these phases retarded the decline of the hardness up to x_{AlN} ~ 0.9. In the (Al,Ti)N coatings deposited by PMS, the formation of w-AlN was avoided up to x_{AlN} ~ 0.65. The Al-rich fcc-(Al,Ti)N phase was apparently stabilized by fluctuations of the Al (and Ti) concentration. The concentration of Al (and Ti) showed almost bimodal distribution in these coatings. In the (Al,Ti)N coatings deposited using SAD, the Al-rich fcc-(Al,Ti)N was stabilized mainly by a low ad-atom mobility, which promoted the formation of supersaturated fcc-(Al,Ti)N.

[1]D. Rafaja, C. Wüstefeld, M. Dopita, V. Klemm, D. Heger, G. Schreiber, M. Šíma, Surf. Coat. Technol. 203 (2008) 572-578]

Keywords: metastable fcc-(Al,Ti)N, microstructure, chemical vapor deposition, spotless arc evaporation, pulsed magnetron sputtering, XRD, TEM

9:20am **B4-3-WeM-5 Oxidation Resistance of AIP Deposited AlCrN and AlTiN Coatings with High Al Compositions***, **Kenji Yamamoto,** H Nii,* Kobe Steel, Ltd., Japan

Al containing transition metal nitrides undergo a characteristic phase transition from cubic B1 to hexagonal B4 structure as the Al content is increased. This change in crystal structure is known to affect not only mechanical property, but also chemical property such as oxidation resistance [1]. AlCrN and AlTiN are one of compounds among such system and applied tribological components such as cutting tool, die and molds for superior mechanical and oxidation resistance at elevated temperatures. A series of AlCrN and AlTiN coating with different Al contents were deposited by cathodic arc ion plating with different substrate bias voltage. Crystal structure of the coatings were examined by XRD and oxidation behavior was investigated by annealing samples in air at 800, 900 and 1000 °C for 30min and surface O composition was measured by EDX and AES for O depth profiling.

Both AlCrN and AlTiN coating showed change in crystal structure depending on the substrate bias, especially Al content is more than 70 at% for AlCrN and 50 at% for AlTiN. These coatings contain hexagonal phase in the coating at low substrate biases and became cubic single phase as the substrate bias is increased. In case of AlCrN, the oxidation behavior seems influenced by the crystal structure and much better oxidation resistance was observed for cubic single phase coating independent of Al content. In case of AlTiN, however, such crystal structure dependent oxidation behavior was not observed. X-ray diffraction analysis of these AlCrN and AlTiN coatings suggests systematic change in grain size corresponding to the change in substrate bias as indicated by width of the diffraction peak. From this observation, it can be concluded that change in oxidation resistance is more likely correlating to the change in grain size of the coating rather than crystal structure.

References:

[1] Reiter et al. Surf. Coat. Technol., Vol. 200, (2005) 2114

9:40am **B4-3-WeM-6 Standing Contact Fatigue Behavior of Nitrided AISI 316L Steels**, ***Daybelis Fernández-Valdés****, A Meneses-Amador, G Rodríguez-Castro, I Campos-Silva,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; A Mouftiez,* ICAM Lille, Matériaux, France*; J Nava-Sánchez,* Tecnologico de Estudios Superiores de Chalco, México

In this work an experimental-numerical evaluation of the standing contact fatigue testing of a nitrided AISI 316L steel is developed. The nitride layers were formed at the surface of a AISI 316L steel by salt bath nitriding process at a temperature of 580 ° C for 1, 3 and 5 hours of exposure time, obtaining three different layer thicknesses. In order to know the mechanical response and the different mechanisms of damage associated with the standing contact fatigue test, Hertzian tests were performed on a MTS machine by cyclic loading of a sphere on a flat surface formed by the layer / substrate system. The standing contact fatigue test was developed through two main stages. Firstly, the critical loads for each treatment condition were determined by monotonic tests, where the appearance of circular cracks were considered as a failure criterion. Subsequently, cyclic subcritical loads were applied at a frequency of 5 Hz. A numerical model based on the finite element method was developed to evaluate the stress field generated in the mechanical contact. The results indicate that the thinner coating exhibits better resistance to standing contact fatigue.

11:00am **B4-3-WeM-10 Effect of Composition on Toughening Mechanism of $V_{1-x}Mo_xN$ Nanocrystalline Thin Film**, ***Yi-Qun Feng****, J Huang,* National Tsing Hua University, Taiwan

The purpose of this study were to investigate the toughening mechanism of $V_{1-x}Mo_xN$ nanocrystalline thin film with different composition of Mo, and compare the texture, residual stress and fracture toughness with each specimen. It is commonly acknowledged that nanocrystalline ceramics with high strength and hardness, while always show low ductility, which limits their applications. Recently, Sangiovanni et al. [1] predicted the $V_{0.5}Mo_{0.5}N$ coating with high hardness and ductility by ab initio density functional theory (DFT), and it has been verified by experiments that $V_{0.5}Mo_{0.5}N$ is more ductile than VN. However, there is lack of studies on the accurate stress and fracture toughness measurements of $V_{1-x}Mo_xN$ and the associated fracture mechanisms. Also it is important to understand the toughness enhancing mechanisms compared with different compositions of $V_{1-x}Mo_xN$. Therefore, this study aimed to investigate the relationship of texture, residual stress and toughness of the different compositions of $V_{1-x}Mo_xN$. $V_{1-x}Mo_xN$ thin films about 1000 nm were deposited on Si substrate by unbalanced magnetron sputtering (UBMS), the compositions of Mo were set to 0.1, 0.2, 0.3, 0.4 and 0.5 by adjusting Mo target currents. After deposition, the ratio of V/Mo and (V+Mo)/N were determined by X-ray photoelectron spectroscopy (XPS), the thickness of all specimens were confirmed by auger electron spectroscopy (AES) and scanning electron microscope (SEM). X-ray diffraction (XRD) was used to characterize the structure and the texture. Besides, the residual stress of the specimens was measured by laser curvature method (LCM) and average X-ray strain (AXS) combined with elastic constant from nanoindentation [2], the hardness was assessed by nanoindentation, and the internal energy induced cracking (IEIC) method was used to evaluate the fracture toughness.

[1] D. G. Sangiovanni, V. Chirita, L. Hultman, Phys. Rev. B, 81 (2010) 104107.

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

11:20am **B4-3-WeM-11 Influence of Mo Contents on Elevated Temperature Tribological Characteristics of CrAlMoSiN Nanocomposite Coating**, ***Yu-Chia Lin****, H Tao, J Duh,* National Tsing Hua University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

CrAlMoSiN nanocomposite coatings were produced by doping Mo into the CrAlSiN nanocomposite matrix via radio frequency magnetron sputtering. CrAlMoSiN thin films with different Mo contents were deposited on both Si-wafer and Inconel-718 substrate by controlling the Mo target working power. Since CrAlSiN nanocomposite coatings exhibit superior high temperature wear resistance, the addition of Mo into CrAlSiN nitride coatings will offer extra self-lubricating characteristic, which leads to lower friction coefficient. By doping Mo in to CrAlSiN coating via composition control, CrAlMoSiN coatings with high temperature wear resistance and reduced friction coefficient could be developed.

The chemical compositions of as-deposited coatings were identified by a FE-EPMA. The tribological property was evaluated by a tribometer with temperature control unit. The wear tracks were analyzed by an Alpha-step to calculate the wear rate. The nano-hardness (HIT) and reduced elastic modulus (EIT*) were examined by a nano-indenter. Further, microstructure of wear tracks was analyzed by FE-SEM and HR-TEM. The phase transformations were observed by a Gazing Incidence XRD and XPS.

11:40am **B4-3-WeM-12 Characterization of Cosputtered W –Si– N Coatings**, ***Yu-Heng Liu,*** National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan*; B Liu, Y Chen,* National Taiwan Ocean University, Taiwan

Monolithic and multilayered W–N and W–Si–N coatings were fabricated through direct current magnetron cosputtering with a nitrogen flow ratio (N_2/(N_2 + Ar)) of 0.4 at substrate holder rotation speeds of 0 and 5 rpm, respectively. The characteristics and oxidation behaviors of the W–N and W–Si–N coatings were investigated by nanoindentation technique, X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. The mechanical properties of crystalline W–N coatings correlated to their texture and residual stress. The monolithic $W_{77}N_{23}$ samples located nearest to the W target exhibited a high deposition rate of 18.0 nm/min, a strong (200) texture coefficient, a high nanoindentation hardness of 32.7 GPa, a high Young's modulus of 392 GPa and a residual stress of −3.2 GPa. The addition of Si into the W–N matrix transformed the coatings to be an X-ray amorphous phase dominated structure comprising constitutions of Si_3N_4, W_2N, and W. The preferential formation of Si_3N_4 declined the residual stress and mechanical properties of the W–Si–N coatings with increasing the Si contents. By contrast, the oxidation resistance was improved by adding a Si content > 24 at.% after annealing at 600 ◦C in a 1% O_2–99% Ar atmosphere.

12:00pm **B4-3-WeM-13 RF Input Power Effect on Microstructure and Mechanical Properties of TaSiN Coatings**, ***Zheng-Xin Lin****, Y Liu, S Wang,* National United University, Taiwan*; M Guillon,* Polytech Lyon, France*; F Wu,* National United University, Taiwan

The TaSiN nanocomposite thin films were fabricated by a reactive radio frequency ,r.f., magnetron sputtering system with pure Ta and Si sources. The Ar/N_2 flow ratio was fixed at 18/2 sccm/sccm, while r.f. input powers for Ta and Si were from 50 to 200W and from 50 to 150W, respectively. The Si contents doped in the coating ranged from 0 to approximately 25 at.%. The plasma of various process conditions were investigated by Optical Emission Spectroscopy.Characterizations by XRD, TEM, SEM revealed the dependence of Si dopeing and SiN_x phases on the preferred orientation, crystalline behavior, microstructure. Mechanical properties through wear tester, Rockwell.C and nano-indentation were evaluated to check the durability, adhesion and hardness, respectively. When the content of silicon reaches 17 at.%, the TaSiN structure evolved from crystallization to amorphous, leading to a significant degradation of mechanical properties. The TaSiN with lower Si contents exhibited TaN with SiN_x phase and processed superior mechanical strength.

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