Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-1

Properties and Characterization of Hard Coatings and Surfaces

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

8:00am **B4-1-1 Thermal Stability and Mechanical Properties of Sub-stoichiometric TiAlN Thin Films***, **Katherine Calamba,*** Linköping University, Sweden*; I Schramm,* Saarland University, Sweden*; M Johansson-Jõesaar,* SECO Tools, Sweden*; J Pierson,* University of Lorraine, France*; M Odén,* Linköping University, Sweden

Aspects on thermal stability of $(Ti_{1-x}Al_x)N_y$ alloys (y<1) were investigated because recent findings show that small amounts of nitrogen vacancies cause significant stability improvement by suppressing detrimental phase transformations, i.e. phase transformation of *c*-AlN to *w*-AlN is delayed to higher temperatures compared to stoichiometric films. The substoichiometric TiAlN alloys were deposited via cathodic arc evaporation technique and the degree of ionization of the arc plasmas was tuned by varying the bias voltage from -30V to -80V. The microstructural evolution and thermal stability of the coatings were examined using transmission electron microscopy, x-ray diffractometry, differential scanning calorimetry, and atom probe tomography. In the as-deposited state, the highly biased films show higher hardness, i.e. the enhanced ion bombardment caused beneficial changes in morphology, microstructure, compressive stresses, and densification. However, at elevated temperature low biased films retain their hardness to higher temperatures compared to high biased films. This behavior is discussed in terms of an enhanced driving force for phase separation in the high biased films caused by self-interstitials, generated by the ion-bombardment during growth, diffusing into the excess vacancies to relive the stress. Such annihilation of defects causes the enthalpy of the system to increase, which promotes phase separation. On the other hand, low biased films with less self-interstitials show the highest phase stability and the age hardening effect was retained to the highest reported temperature to date for the Ti-Al-N material system. Our study shows that varying the nitrogen vacancy concentration of transition metal nitride thin films offers a mean to tune of thermal stability and mechanical properties for hard coating applications.

8:20am **B4-1-2 Microstructure and Hardness of Ti-B-N-C Nanocomposites Deposited from Ti and B_4C Targets***, **Christina Wüstefeld,*** Institute of Materials Science, TU Bergakademie, Germany*; M Motylenko,* Institute of Materials Science, TU Bergakademie Freiberg, Germany*; M Síma, M Jílek,* SHM Ltd., Czech Republic*; D Rafaja,* Institute of Materials Science, TU Bergakademie Freiberg, Germany

The addition of boron to titanium nitride during the deposition of the Ti-B-N based coatings is known to facilitate the formation of nanocomposites with excellent thermal stability and very high hardness that are required for special machining applications. The Ti-B-N-based nanocomposites investigated in this study were deposited by using a combination of cathodic arc evaporation (operating with a Ti cathode) and magnetron sputtering (operating with a B_4C cathode). The amount of boron in the coatings was controlled by the magnetron power and the [B]/[N] ratio by the nitrogen flow in the working atmosphere. An additional parameter of the deposition process was the bias voltage, which influences mainly the kinetic energy of titanium ions.

The indentation experiments have shown that all deposition parameters, i.e., the magnetron power, the nitrogen flow and the bias voltage, strongly influence the hardness of the Ti-B-N-C nanocomposites. In order to be able to explain the observed correlation between the deposition parameters and the hardness of the coatings, the phase composition, the distribution and morphology of individual phases, the size and preferred orientation of crystallites and the residual stress were investigated by using a combination of glancing-angle X-ray diffraction (GAXRD), transmission electron microscopy with high resolution (HRTEM) and electron energy loss spectroscopy (EELS). The correlations between individual microstructure parameters like distribution of individual phases, morphology of crystallites or grains, preferred orientation of crystallites and residual stresses are discussed. The residual stress was measured via sample bending and by modified $\sin^2\psi$ method (GAXRD). The residual stresses obtained from the complementary methods will be compared.

8:40am **B4-1-3 Strategies for Fracture Toughness Enhancement of Nanostructured Films by Microstructural and Grain-boundary Design: The Role of Microstructure, Stress and Property Heterogeneity***, **Rostislav Daniel,** C Mitterer, J Keckes,* Montanuniversität Leoben, Austria **INVITED**

In nature, extraordinary material properties are achieved by combining hard and soft or stiff and elastic constituents, which form very tough, hard and damage resistant architectures. The key for these outstanding properties is the variation in material microstructure and mechanical property distributions over large scales. In this paper, the inherent advantages of these principles will be demonstrated for nanostructured brittle thin films with the aim to establish a universal concept for improvement of fracture behavior of materials where a lack of plasticity compromises their application for surface protection despite their high strength and thermal stability. Besides strategies to enhance fracture toughness by transformation toughening, coherency strain or intrinsic compressive stress, the main focus will be on microstructural design of thin films to control crack formation and propagation. The microstructure- and property-dependent mechanisms controlling crack propagation (e.g. deflection by weak interfaces or crack path tortuosity) with subsequent toughness enhancement will be discussed in detail for various material combinations. Microstructurally and mechanically heterogeneous films including representative hard/soft crystalline/amorphous and crystalline/crystalline materials such as CrN/Cr, TiN/SiO_x and AlCrN, characterized with respect to their stiffness, fracture stress and toughness by micromechanical testing of microcantilever beams, will be some of the examples. In addition,special attention will be paid to a new strategy for fracture toughness enhancement by grain-boundary orientation and interface engineering, where crack propagation is inhibited by deflection of cracks at interfaces of columnar grains designed with chevron-like architecture and combined with elastic interlayers. In this way, even common nanocrystalline brittle materials may exhibit considerably enhanced plasticity.

9:20am **B4-1-5 Epitaxial Growth of HfN Films using Synchronized Pulsed Substrate Bias during HiPIMS Discharge***, M Villamayor,* Linköping University, (IFM), Sweden*; T Shimizu,* Tokyo Metropolitan Univeristy, Japan*; **Julien Keraudy,** R Boyd,* Linköping University, (IFM), Sweden*; D Lundin,* LPGP, France*; U Helmersson,* Linköping University, (IFM), Sweden

Low-temperature epitaxial growth of high quality transition metal nitride materials is considered so far as one of the great challenges in advanced thin film technology. In this study, we demonstrate that low-energy-ion irradiation at the growth surface during high power impulse magnetron sputtering discharge (HiPIMS) is one of the most promising and widely applicable concepts to deposit stoichiometric, single-crystal HfN films on MgO(001) in the absence of applied substrate heating. The key point of this process is the appropriate selection of the chemical nature of the incident ions, *i.e*, inert gas vs. metal. To control the nature of the ion irradiation, two approaches have been chosen and have consisted to change the nature of the sputtering gas, Ar and Kr, and the time domain to apply substrate bias either continuously (DC) or synchronous in the last moment of the HiPIMS pulse (60 µs after the initiation of the pulse). The substrate bias was set at -60 or -100 V with a pulse width of 100 µs. *In situ* mass spectrometer measurements reveal that, by changing the gas atmosphere from Ar/N_2 to Kr/N_2, the last moment of the HiPIMS pulse evolved from a N^+-dominated phase to Hf^+-dominated phase. High-resolution x-ray diffraction, ω-2θ, azimuthal ϕ scans and reciprocal lattice maps combined with high-resolution cross-sectional transmission electron microscopy analysis established that switching from N^+ to Hf^+ bombardment, as well as switching from DC to pulse synchronized bias, help to promote the growth of fully-relaxed epitaxial HfN layers with an enhancement of the crystallinity by reducing the density of residual point defect.

9:40am **B4-1-6 HiPIMS and Ni Doping Induced Structure Reinforcement and Phase Change in nc-TiC/a-C:H Coatings***, **Pavel Soucek,** J Daniel, J Hnilica, K Bernatova, L Zabransky,* Masaryk University, Czech Republic*; V Bursikova,* Masaryk Univerisity, Czech Republic*; M Stupavska, P Vašina,* Masaryk University, Czech Republic

Nanocomposite coatings consisting of nanocrystallites embedded in an amorphous matrix such as nc-TiC/a-C:H can be tailored to exhibit an unusual combination of properties such as high hardness and modulus combined with low friction and wear. These coatings are usually deposited utilizing direct current magnetron sputtering (DCMS) leading to low ionization of the sputtered titanium. High Power Impulse Magnetron Sputtering (HiPIMS) depositions usually lead to much higher ionization of the sputtered titanium which can alter the deposition process and in turn the properties of the deposited nc-TiC/a-C:H coatings. Using HiPIMS it was possible to make arc-free deposition of coatings with much higher carbon content (> 90 at.%) which was impossible for DCMS. When DCMS was employed black carbon layers were created on the target including the racetrack, whereas HiPIMS employment led to a much cleaner target. This was due to significant ionization of sputtered titanium and its back attraction to the target in HiPIMS. This proved to be highly advantageous for deposition of coatings with high carbon content with regards to arc occurrence and moreover the deposition rate of carbon rich coatings was higher for HIPIMS compared to DCMS. Lower fraction of the a-C matrix phase was found to be created in HiPIMS deposited nanocomposite coatings with < 55 at.% of carbon as compared to DCMS deposited coatings. HiPIMS deposited coatings also exhibited better stoichiometry of the TiC grains. This shows that HiPIMS ensured carbon incorporation into TiC grains rather than forming of a-C matrix. Lower amount of a-C matrix corresponded with smaller mean grain separation distance of the TiC grains by the a-C matrix. This enhanced the nanocomposite grain boundary strengthening leading to overall higher hardness of HiPIMS deposited coatings compared to those deposited by DCMS. HiPIMS deposited coatings also exhibited lower lattice parameter. The crucial parameters for obtaining hardest coatings were found out to be the TiC grain stoichiometry and small mean grain separation by the a-C matrix corresponding to only a few monolayers of the matrix between the grains. HiPIMS utilization favored this structure enhancement making it a promising method of nc-TiC/a-C:H coating preparation. Ni doping led to Ni incorporation into the grains. The grain size as well as the mean grain separation was smaller and the surface features were refined. Thus doping by weak carbide forming Ni can also be used as tool for fine tuning of structure of nc-TiC/a-C:H coatings.

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10:00am **B4-1-7 Correlation of Plasma Parameters and Thin Film Properties of HiPIMS Al-Cr-N films using a Combinatorial Approach***, **Lars Banko**, D Grochla, S Ries, P Awakowicz, A Ludwig,* Ruhr-Universität Bochum, Germany

HiPIMS power supplies provide a variety of settings to tune the plasma in PVD processes. In this work, the direct influence of plasma properties like ion energy, ion flux and electron density on coating features like microstructure and mechanical properties was investigated.

Single phase fcc - Al-Cr-N films were deposited at 500°C by reactive co-deposition of Al und Cr in N_2/Ar – plasma. Continuous composition materials libraries ((Al_{100-x} -Cr_x)-N (0.4 < x < 0.9)) were synthesized by confocal alignment of two 4 inch cathodes. Both cathodes were powered by HiPIMS with an average power of 200 W. The pulse length was kept constant at 40 µs. Three depositions with frequencies of 100, 200 and 400 Hz were carried out resulting in a variation of peak power (0.3 – 2.5 kW/cm^2) and peak current density (0.5 – 3.8 A/cm^2).

Time- and space-resolved plasma diagnostics were applied to characterize ion energy, ion flux and electron density at five positions corresponding to different compositions. The electron density was investigated using Langmuir probe and the ion energy distribution function was determined by retarding field energy analyzer. Without additional bias, maximum ion energies of 70 eV were measured. The mean ion energy was found to vary between 4.5 and 9 eV, depending on the applied frequency.

The materials libraries were characterized regarding microstructure, morphology, composition, hardness, Young's modulus and residual stress. The residual stress was measured on 120 µm thick micro-cantilever stress sensors. By thermal cycling of the sensors after the deposition, intrinsic and extrinsic stress components could be determined separately.

The results of this investigation clearly show the influence of ion energy and ion flux on composition, microstructure and morphology and thereby on mechanical properties like residual stress and hardness. The effect of ion flux and ion energy on the materials properties are amplified by increasing Al-concentration.

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