Hard Coatings and Vapor Deposition Technologies
Room Golden State Ballroom - Session BP-ThP

Hard Coatings and Vapor Deposition Technologies (Symposium B) Poster Session

BP-ThP-1 Influence of Various Tool Steels and Cemented Carbide on Growth of PVD Hard Coatings*, K. Bobzin, C. Kalscheuer,* ***Marco Carlet (carlet@iot.rwth-aachen.de)****, D. Hoffmann,* RWTH Aachen University, Germany

In order to pursue lightweight construction, components are manufactured with high-strength materials. On the tool side, this leads to increased tool wear, e.g. on the punches of fine blanking tools. For this reason, high-strength and tough tool steels produced by powder metallurgy (PM) are increasingly used. Furthermore, PVD hard coatings are applied to increase tool life. In this study, the influence of the alloying elements as well as the manufacturing method of tool steels, whether powder or melt metallurgical (MM), is investigated on the coating growth and morphology. For this purpose, PVD hard coatings, particular the nanocomposite TiAlCrSiN, was deposited on various tool steels using an industrial coating unit. In the current study, PM and MM high speed steels (HSS) as well as MM cold work, hot work and plastic mold steel substrates were taken into account. In addition, cemented carbides were used as reference substrate material. Moreover, the influence of a TiAlN interlayer on the growth of the nanocomposite TiAlCrSiN toplayer is analyzed. The deposition of a CrAlN coating was investigated as reference to the nanocomposite. Confocal laser scanning microscopy (CLSM) and scanning electron microscopy (SEM) were used to analyze the coating topography. The coating morphology was examined by SEM and the crystal structure by X-ray diffraction (XRD). The indentation hardness and modulus were determined by nanoindentation. It can be seen that the coating growth of TiAlCrSiN is strongly dependent on the manufacturing process of the tool steel. On the PM HSS, the TiAlCrSiN coating exhibits a significantly rougher topography compared to all investigated melt metallurgical steel substrates and cemented carbide. Furthermore, it is evident in cross-sectional micrographs that the otherwise fine-crystalline, homogeneous morphology of the TiAlCrSiN coatings from the PM HSS substrate material exhibit cone-shaped grains. In addition to the nanocomposite TiAlCrSiN, the coating system CrAlN was deposited. Compared to the TiAlCrSiN nanocomposite, the CrAlN coating reveals no significant differences depending on the substrate materials. The findings can support the selection of suitable combinations of substrate materials and PVD hard coatings to improve tool life. In this work, it was shown that the coating growth of the PVD nanocomposite TiAlCrSiN is significantly dependent on the substrate material, in contrast to the ternary coating system CrAlN. Furthermore, the substrate influence of the coating growth cannot be suppressed by the prior application of an interlayer.

BP-ThP-2 Influence of Deposition Parameters on Chemistry, Structure and Mechanical Properties of Vanadium Carbide Thin Films*,* ***Barbara Schmid (barbara.schmid@tuwien.ac.at)****, N. Koutná,* TU Wien, Institute of Materials Science and Technology, Austria*; E. Halwax,* TU Wien, Austria*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Cubic transition metal carbides generally exhibit high melting points as well as high hardness, which makes them especially interesting for the application as protective coatings. Vanadium carbide (VC) is not an exception to this trend with a melting point above 3000 K and up to 40 GPa in hardness.

However, the non-reactive synthesis of VC_x via DC magnetron sputtering is rare. The variation of deposition parameters such as working gas pressure (here, Ar), gas flow and sputtering power density applied to a stoichiometric VC compound target can result in drastically different thin film materials.

Varying these deposition parameters allowed to synthesise VC_x thin films with different chemistry, microstructure, as well as indentation hardness and modulus.

These material characteristics were investigated using electron probe microanalysis, X-ray diffraction, scanning and transmission electron microscopy, and nanoindentation. The obtained variation in lattice parameter and indentation modulus have been compared to density functional theory data for stoichiometric and non-stoichiometric VC_x. This allowed us to draw a clear picture of the deposition–structure–property relations for VC_x.

BP-ThP-3 Influence of High-Power Pulse Magnetron Sputtering Tantalum Nitride Film Characteristics and Protection Behavior*,* ***Yung-Chi Chang (vicky5062823@gmail.com)****, S. Hsu, C. Tu, D. Hong, F. Wu,* National United University, Taiwan

Nowadays quality requirements, such as higher hardness, wear resistance, sufficient toughness, adhesion strength and so ow, are focused for transition metal nitride, TMN, hard coating field. The selection of coating among various possible materials and related manufacturing processes is quite a challenge and requires careful consideration on the functions in the development systems. Among TMNs, with high hardness excellent tribological behavior, thermal and electrical performance, TaN. Has been chosen as a good protective layer for working components in versatile applications. In this study, and the enysfalline and metastable amorphous phase of tantalum nitride are fabricated using radio frequency, r.f., reactive magnetron sputtering technique. A multilayer film formed by alternating stacking of the above mentioned crystalline/amorphous layers is deposited through input power and gas inlet control. The adhesion of the tantalum nitride film is studied and compared with controlling parameters of interlayers with changes thickness, r.f. power, and high intensity power plasma. Compared with r.f., the single-layer film has a compact structure due to the higher energy of plasma power. The higher energy deposition, improves the crystallinity, and lead to a larger grain size. At the same time, the surface roughness of the film is reduced, and the hardness and Young's modulus are improved. The multilayer film is manufactured through the crystalline/amorphous stacking, the hardness and Young's modulus and wear resistance are superior than those of the single-layer film.

Keywords : HiPIMS, sputtering, TaN, multilayer

BP-ThP-5 Rotating Spokes in Reactive HiPIMS Process Measured by Spatially Resolved OES*,* ***Marta Šlapanská (slapanska@physics.muni.cz)****, M. Kroker, J. Hnilica, P. Klein, P. Vašina,* Masaryk University, Czechia

The rotating plasma patterns, also known as spokes, spontaneously appearing in E × B magnetised plasma discharges, such as Hall thruster and high power impulse magnetron sputtering (HiPIMS) discharge, have been thoroughly investigated mainly in the non-reactive atmosphere under many different experimental parameters. Among other things, it has been discovered that the presence of spokes enhanced the transport of sputtered species from the target to the substrate, leading to a much more energy-efficient HiPIMS process. Due to the reactive processes being widely used in industry, there is an effort to find out more information about spokes in reactive atmospheres and their effect on the deposition process and the transport of sputtered species at those conditions. The use of spatially resolved optical emission spectroscopy in a single-shot mode is one of the possibilities for a deeper understanding of the spokes.

In this contribution, the non-invasive spatial-resolved OES of the spoke was conducted in reactive HiPIMS discharge. The HiPIMS pulses were 100 µs long with a repetition rate of 5 Hz. The 3-inch titanium target, argon as working gas, and nitrogen as reactive gas were utilised. The constant total pressure was set to 1.0 Pa. Different reactive gas flows were applied to measure the properties of spokes in both metallic and poisoned modes.

The fast photodiode and the Langmuir probe were used to capture and determine the position of the passing spoke. The signals from the photodiode and the Langmuir probe were synchronised with the spectrometer and an ICCD camera. The ICCD camera possesses a dual-image-feature mode, which allows capturing two consecutive images with only a 1.5 µs delay between them. It enabled to determine the spoke propagation velocity. The single-shot measurements ensured that one waveform and one double image were acquired simultaneously from a single HiPIMS pulse for each spectrum. The spatial-resolved emissions of argon, nitrogen, and titanium atoms and ions spectral lines were investigated within the spoke passing by the probes.

BP-ThP-6 Sputtered Amorphous Carbon Interlayers for Homogeneous Lithium Plating and Stripping in Solid-State Batteries*, T. Amelal, M. Futscher, J. Patidar, A. Müller, A. Aribia, Y. Romanyuk,* ***Sebastian Siol (sebastian.siol@empa.ch)****,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Recently, it was shown that the introduction of an amorphous Ag-C composite into solid-state batteries can lead to increased long-term stability.[1] However, the reason why the interlayer shows this advantageous behavior is not well understood.

We deposit thin carbon interlayers between current collector and solid electrolyte by two physical vapor (PVD) deposition techniques. By using direct current magnetron sputtering (DCMS) and high power impulse magnetron sputtering (HiPIMS) the kinetic energy of the incident ions can be tuned over a wide range. This allows us to independently vary the density, conductivity, and microstructure of the carbon interlayers.

We show the influence of different material properties of the carbon interlayer on lithium plating and stripping using copper as the current collector and lithium phosphorus oxynitride (LiPON) as the solid electrolyte. We find that the amorphous carbon interlayer reduces the overpotential for lithium plating and increases the critical current density for lithium plating and stripping up to 8 mA/cm^2. We further show that the initial lithium loss due to interphase formation and the critical current density strongly depends on the morphology and the electrical conductivity of the carbon interlayers. Finally, we investigate the role of Ag by introducing different amounts of Ag into the amorphous carbon interlayers. Our results shed light on the key factors that enable homogeneous lithium plating and thus the use of lithium metal in solid-state batteries.

[1] Y.-G. Lee et al. High-energy long-cycling all-solid-state lithium metal batteries enabled by silver–carbon composite anodes. Nat. Energy 5, 299–308 (2020)

BP-ThP-9 e-Poster Presentation: Effect of Precursor Interactions on Film Growth Rate and Properties in Chemical Vapor Deposition of $Hf_{1-x}Al_xB_2$ Alloy Films*, Kinsey Canova (kcanova2@illinois.edu)**, S. Shrivastav, C. Romnes, D. Yun, J. Krogstad, J. Abelson,* University of Illinois at Urbana-Champaign, USA

HfB_2 coatings impart excellent surface hardness and low sliding friction, but the service life in air at moderate temperatures is reduced by the formation of boron oxide, which is lost to evaporation.Addition of Al is one possible route towards oxidation resistance, if the surface can form an Al_2O_3 surface layer that impedes further oxygen transport. (We report oxidation studies elsewhere in this conference.)

We use low temperature chemical vapor deposition (CVD) to grow $Hf_{1-x}Al_xB_2$ alloy films from two precursors, $Hf(BH_4)_4$ and Me_3N-AlH_3 (TMAA).We show that TMAA flux accelerates the reaction rate of the $Hf(BH_4)_4$, but that a flux of the TMAA byproducts, including Me_3N, inhibits the growth rate of HfB_2. In the former case, we will present evidence towards which chemistry is involved in the growth acceleration, whether it be precursor-precursor interaction or another precursor-byproduct interaction; high byproduct pressures for these experiments can be sustained within a deep trench or under slow pumping.These results imply a feedback loop in the film growth rate, where the accelerated deposition due to TMAA is opposed by a progressive increase in the Me_3N inhibitor pressure, which may dampen the acceleration effect.

We uncouple these interactions using two distinct CVD chambers.The conventional CVD chamber is rapidly pumped, and the alloy growth rate is found to be a steady-state function of the precursor fluxes and substrate temperature (surface reaction rates).The other CVD chamber is unpumped (static), which allows the use of very high precursor pressures to amplify the effects of precursors and byproducts. We interpret these results in the context of accelerating and inhibiting interactions that we have measured in other chemistries, and we then show how the growth rate affects film stability, density, and composition.

BP-ThP-13 Biocompatibility Evaluation of nc-TiC/a-C:H Nanocomposite Diamond-like Carbon Coatings: Effect of Carbon Content*, B. Lou,* Chang Gung University, Taiwan*; Y. Hsiao, L. Chang,* Ming Chi University of Technology, Taiwan*; M. Ger,* National Defense University, Taiwan*; **Jyh-Wei Lee (jefflee@mail.mcut.edu.tw)**,* Ming Chi University of Technology, Taiwan

The nc-TiC/a-C:H nanocomposite diamond like carbon (DLC) coating has been studied due to its good mechanical properties, corrosion resistance and biocompatibility. In this work, four nc-TiC/a-C:H coatings with different carbon contents were grown by a superimposed high power impulse magnetron sputtering (HiPIMS) and medium frequency (MF) coating system utilizing a plasma emission monitoring feedback control. The target poisoning ratio ranging from 80% to 95% and the gas flow rate of acetylene were controlled by a plasma emission monitoring (PEM) system. The chemical composition, crystallinity, hardness, wear resistance, adhesion and surface roughness values of coatings were investigated. Furthermore, the in vitro biocompatibility of MG 63 human osteoblast-like cells and the migration ability of HaCaT keratinocyte cell on selected DLC coatings were also evaluated, respectively. The sensitization test of DLC coatings was conducted by the in vivo animal test using the subcutaneous implantation of DLC coated 316L SS disks on the back of SD rats. The pathological changes and inflammation of tissues after the subcutaneous implantation were explored.

In this work, the hardness and elastic modulus of four DLC coatings fabricated from 80% to 95% target poisoning ratios were higher than 14 GPa and 120 GPa, respectively. The wear rates of four DLC coatings were all lower than $10^{-6} mm^3/N/m$ with coefficient of friction values less than 0.25. Meanwhile, very good cell adhesion, free of toxicity, good cell migration (**Fig.1**) and proliferation ability, and free of sensitization in animal body were achieved for two nc-TiC/a-C:H DLC films (TiC80 and TiC90) deposited at 80% and 90% target poisoning ratios, which can be further deposited on the 3-dimensional surfaces of surgical instrument, such as surgical blades and xysters.

Keywords: nc-TiC/a-C:H nanocomposite diamond like carbon coating, HiPIMS, in vitro MG63 cell test, in vitro cell migration test, subcutaneous implantation in vivo animal test

BP-ThP-14 TiN/TaN Superlattice Films Improved by Interfacial Dopings*, **Zecui Gao (zecui.gao@tuwien.ac.at)**, N. Koutná, J. Buchinger, T. Wojcika, P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The superlattice architecture, characterized by different nanolayered materials that are alternatively and coherently stacked, allows to stabilize metastable phases and optimize typically antagonistic properties of ceramic coating materials, such as hardness and fracture toughness. As rocksalt-structured TiN and $Ta_{0.5}N$ (featuring metal vacancies) have significant elastic differences, they promise a pronounced superlattice (SL) effect. TiN/Ta_xN films were thus deposited with a ~5 nm bilayer period by DC reactive magnetron sputtering. As expected, the SLs show a higher hardness (32.9 GPa) than monolithic TaxN (30.1 GPa) and TiN (28.5 GPa), with an intermediate indentation modulus of 425.0 GPa ($Ta_{0.5}N$ 379.9 GPa and TiN 529.7 GPa).

As established by previous studies, the improved hardness is partly due to the hindrance of dislocation movement across interfaces. Thus, we implement atomic quantities of Si/C/B in between all layers of TiN/Ta_xN SLs to further enhance the interlayer boundaries. All of the doped superlattice coatings show exceptional hardness properties and improved epitaxial growth on MgO compared to the doping-free SL. Especially, the TiN/Si/Ta_xN film produced the highest hardness of ~40.7 GPa, and the TiN/B/Ta_xN film produced the highest fracture toughness of ~4.11 MPaÖm. Overall, they possess promising hardness and Fracture toughness compared favorably to their monolithic building blocks and TiN/Ta_xN SL.

BP-ThP-16 Fifty Shades of TiN: How Deposition Conditions Influence the Growth Morphology and Thereby Hardness and Especially Fracture Toughness*, **Paul Mayrhofer (paul.mayrhofer@tuwien.ac.at)**, R. Hahn, B. Hajas, A. Kirnbauer,* TU Wien, Austria

About fifty different TiN coatings were prepared by reactive and non-reactive magnetron sputtering, as well as by reactive cathodic arc evaporation. In addition to vary between these three individual deposition techniques, we also individually varied the substrate temperature, partial pressures, substrates (e.g., Si(100), MgO(100)(110)(111), sapphire), substrate-to-target distance, as well as bias potential. The fracture toughness of these individually prepared TiN coatings was evaluated from micromechanical bending tests (inside a FEGSEM) of free-standing cantilevers. The individual deposition techniques and conditions result in either pronounced columnar or rather dense growth morphologies, with open or compact column and grain boundary regions, or epitaxially grown single-crystals. Due to these variations in growth morphology, the hardness (obtained by nanoindentation) of TiN varied between 15.9 and 33.9 GPa and their fracture toughness between 0.6 and 2.9 MPa√m.

We will have a closer look on the overall correlation between growth morphologies, preferred orientation, residual stresses, and mechanical properties. But also, how a subsequent vacuum annealing treatment (to mimic application at elevated temperatures) influences these characteristics.

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