Hard Coatings and Vapor Deposition Technologies
Room On Demand - Session B5

Hard and Multifunctional Nanostructured Coatings

B5-1 INVITED TALK: PVD of Hard Nanocomposite Coatings Using Multiphase SHS Cathodes - Evolution and New Horizons*, Philipp* ***Kiryukhantsev-Korneev (kiruhancev-korneev@yandex.ru)****, E. Levashov,* National University of Science and Technology "MISiS", Russian Federation **INVITED**

The development of PVD technologies is often related with creation of new multicomponent materials that are used as precursors in deposition process. Particularly relevant is the manufacture of cathodes made of ceramics & composite materials. Since the doping of coatings by structure modifiers, such as B or Si, for example, is a non-trivial task. Among the methods of ceramic cathodes manufacturing can be noted the pressing+sintering & hot pressing technology. Self-propagating high-temperature synthesis (SHS) is the cost effective & convenient method for manufacturing of composite cathodes [1].

The SHS method allows obtaining a wide range of materials & cathodes have a high density & a low content of impurities due to self-cleaning effect in the combustion wave. In present review, the several types of advanced coatings deposited with the SHS-materials were demonstrated.

It was shown that the follow nanocomposite coatings can be produced in various energy regimes, including rigid, due to the use of functionally graded & reinforced SHS-materials (FGM & RM):

a) hard oxidation resistant MoHfSiB, MoZrSiB, & TaZrSiB coatings were obtained by DC magnetron sputtering (MS) & pulsed MS of ($MoSi_2$-HfB_2-MoB)/Mo, ($MoSi_2$-ZrB_2-MoB)/Mo, & (ZrB_2-$TaSi_2$)/Mo FGM disk targets [2] b) hard optically transparent TaSiCN coatings - by MS of $TaSi_2$-TaC-SiC-Si_3N_4 RM disk targets c) hard corrosion resistant CrB_2 & TiAlNiCN coatings - by HIPIMS using CrB_2 & TiC-NiAl disk targets [3]. d) hard wear resistant TiCrBN coatings - by ion implantation (MEVVA) or pulsed cathodic arc evaporation (PCAE) of (TiB-Cr_4Ti_9B-Cr_2Ti)/(Ti+TiB) ring FGM targets [4]. e) hard oxidation & corrosion resistant coatings - by PCAE method using CrB_2 & Cr_3C_2-NiAl rod targets. f) hard TiAlSiCN & TiCrSiCN coatings with high thermal stability/oxidation resistance - by MS of $TiAl_3$-TiC-Ti_5Si_3-AlN & TiC-Cr_3C_2-Ti_5Si_3 disk targets at high currents [5]. g) hard wear resistant soft magnetic FeTiB films - by MS of Fe/TiB_2 segment target [6] h) hard oxidation resistant SiBCN films - by ion sputtering (IS) & MS of SiC-B_4C disk SHS-targets [7].

The research was carried out under the financial support of the Russian Science Foundation in the framework of project No. 19-19-00117.

1. E.A. Levashov et al. Int Mater Rev 62 (2017) 203

2. Ph. Kiryukhantsev-Korneev et al. Corros Sci 123 (2017) 319

3. Ph. Kiryukhantsev-Korneev et al. Ceram Int (2019) doi.org/10.1016/j.ceramint.2019.09.152

4. Ph. Kiryukhantsev-Korneev et al. J. Phys.: Conf. Ser. 1238 (2019) 012003

5. K. Kuptsov et al. Acta Mater 83 (2015) 408

6. E. Sheftel et al. Phys Status Solidi 13 (2016) 965

7. Ph. Kiryukhantsev-Korneev et al. Prot Met Phys Chem 53 (2017) 873

B5-3 On the Structure and Mechanical Properties of X_2BC Coatings Prepared by High Power Impulse Magnetron Sputtering at Different Temperatures*, Pavel Soucek (soucek@physics.muni.cz)****, M. Polacek, L. Zabransky, M. Stupavska, P. Vasina,* Masaryk University, Brno, Czech Republic

As the demands for the quality and speed of machining increase, the application of protective coatings on cutting or forming tools becomes increasingly important. Currently used protective coatings exhibit sufficient hardness, but this trait is often coupled with distinct brittleness. Recently a material combining seemingly mutually exclusive high hardness and moderate ductility has been theoretically predicted [1]. This material contains atoms of a transition metal (X), boron (B) and carbon (C) in X_2BC stoichiometry ordered in a complex high aspect ratio unit cell. The arrangement of the unit cell provides for high hardness of the material due to strong ionic-covalent bonds together with enhanced ductility owing to planes with only metallic bonds providing for plastic deformation of the cell. The properties of X_2BCs with different transition metals were calculated; however, experimental synthesis of only crystalline Mo_2BC was reported so far [2,3]. Apart from post-deposition annealing [3], HiPIMS was shown to be an effective way to prepare crystalline Mo2BC at industrially relevant deposition temperatures [2]. Other X_2BC such as W_2BC have been predicted to exhibit better mechanical properties compared to Mo_2BC, however, this comes at the cost of near-zero formation enthalpy predicting problems with the crystallization of this phase. On the other hand, systems such as Nb_2BC should exhibit lower hardness and ductility, but they should be significantly easier to be synthesized in the correct crystalline form.

This contribution reports on HiPIMS driven deposition of different X_2BC systems covering systems with low as well as higher negative formation enthalpies. Coatings prepared at ambient temperature as well as those prepared elevated temperatures > 700 °C will be compared. The correlation between the deposition parameters, the structure of the coatings and their mechanical properties will be shown.

This research has been supported by the project LO1411 (NPU I) funded by Ministry of Education, Youth and Sports of Czech Republic, project CZ.1.05/2.1.00/03.0086 funded by the European Regional Development Fund and GACR project 15-17875S.

[1] H. Bolvardi, J. Emmerlich, M. to Baben, D. Music, J. von Appen, R. Dronskowski, J.M. Schneider, J. Phys.: Condens. Matter 25 (2013) 045501

[2] H. Bolvardi, J. Emmerlich, S. Mráz, M. Arndt, H. Rudigier, J.M. Schneider, Thin Solid Films 542 (2013) 5-7

[3] L. Zábranský, V. Buršíková, P. Souček, P. Vašina, J. Dugáček, P. Sťahel, J. Buršík, M. Svoboda, V. Peřina, Vacuum 138 (2017) 199-204

B5-4 Ammonium Thiosulfate Precursor for Coating Molybdenum Disulfide onto the Surface of Porous Metal for High Anti-Wearing Application in the Machinery Industry*, Lung-Hao Hu (lunghhu@g-mail.nsysu.edu.tw)**,* National Sun Yat-Sen University, Taiwan*; P. Chen,* Southern Taiwan University of Science and Technology, Taiwan

High anti-wearing capability of friction coating is extremely important to any low friction and machinary industry, especially for highly automated production era coming, "Industry 4.0". Molybdenum disulfide (MoS_2) belongs to Transition-metal dichalcogenids, TMDs . It is composed of layered structures, providing excellent wear resistance due to layer sliding . In this study, a cheap and massive producible ammonium thiosulfate precursor ($(NH_4)_2MoS_4$) has been developed for coating MoS_2 layer onto the nano-porous anodic aluminum oxide (AAO) layer on the surface of 7003 series aluminum alloy. MoS_2 layer on the aluminum alloy surface is detected by scanning electron microscope (SEM). The ammonium thiosulfate precursor is pyrolyzed at 280, 375, 400 and 550°C, respectively to form the MoS_2 layer. The wearing experiment is tested by using the Surface Hardness Abrasion Tester. After 1440 m wear test, the wear rates (weight loss/original weight) of pure 7003 aluminum alloy, AAO and MoS_2 coated aluminum alloy pyrolyzed at 400°C are 0.339%, 0.017%, 0.0109%, respectively. The thickness of the molybdenum disulfide film sliced and observed by focused ion beam-transmission electron microscope (FIB-TEM) is about 40 nm. The surface hardnesses of AAO and MoS_2 coated aluminum alloy are 3~4 GPa and 5~6 GPa, respectively, measured by nanoindentation. As the result of the test, the coating of MoS_2 layer on the surface of aluminum alloy substantially enhances anti-wear capability and hardness. This coating technique is expected to be used in all kind of metal parts for improving the lifetime of automated equipment .

B5-5 Optimization of TiSiCN Coating Properties Obtained by RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering*,* ***Joël Matthey (joel.matthey@he-arc.ch)****,* Haute Ecole Arc Ingenierie HES-SO, Switzerland Ecole Arc Ingenierie, Switzerland*; O. Banakh, R. Constantin, F. Bisoffi, M. Erard,* Haute Ecole Arc Ingenierie HES-SO, Switzerland

Recently, remarkable properties of the TiSiCN coatings namely low friction and good wear protection have been reported. Our study aimed at a comparison between different technologies (RF Magnetron Sputtering and High Power Impulse Magnetron Sputtering) used for the coating depositions. Operating in RF mode, a composite target Ti-Si-C was sputtered in Ar + N_2 atmosphere. In HiPIMS mode, the coatings were obtained from alloyed TiSi targets with different Si contents (15 and 25 at.%) in a gas mixture containing Ar + N_2 + C_2H_2. Tailoring the coating properties can be successfully performed with a help of the target ion-induced secondary electron emission (ISEE). Technical aspects of both technologies will be discussed in order to set a relationship between thin film properties and process parameters. Physicochemical analyses (XRD, SEM, XPS and RBS) were carried out to evaluate the coating composition, morphology and crystalline structure. Residual stresses were determined by the curvature method on glass plates. Nanohardness values up to 28 GPa and Young's modulus values up to 216 GPa were obtained while the coefficient of friction exhibited values below 0.35 against steel in an unlubricating pin-on-disk setup. The process parameters have been optimized to maximize the ion bombardment of the substrate surface by a monitoring the bias current signal with a Rogowski coil probe. The coating thickness was set to one micron onto polished steel substrates.

B5-6 Characteristics of Hf(*M*)SiBCN (*M* = Y, Ho, Ta, Mo) Coatings: Role of the *M* Choice*, **Martin Matas (matasma@kfy.zcu.cz)**, M. Prochazka, J. Vlcek, J. Houska,* University of West Bohemia, Czech Republic

Thin films based on light main group elements are attractive due to a unique combination of properties ranging from high hardness through optical transparency to high–temperature stability and oxidation resistance. The properties, in the first place electrical conductivity, can be further modulated by addition of early transition metals. Properties of amorphous Hf(*M*)SiBCN films are investigated by combining their preparation using pulsed magnetron sputtering of boron–rich composite targets B_4C–Hf–*M*–Si (45–65% B_4C, 15–20% Hf, 5% Y/Hf/Ho/Ta/Mo, 15–30% Si) in 85% Ar + 15% N_2 discharge gas mixture with *ab-initio* calculations. First, we study the effect of the *M* choice and fraction on calculated mechanical properties and formation energy (E_{form}) of binary *M*N and ternary $Hf_xM_{1-x}N$ crystals. We discuss the dependence of E_{form} on the crystal structure and on the distribution of Hf and *M* in the metal sublattice. The calculated mechanical properties of *M*N (rather than $Hf_xM_{1-x}N$) very well correlate with measured mechanical properties of a–Hf*M*SiBCN. The driving force towards N incorporation, monotonically decreasing with increasing periodic-table group number of *M* according to the calculated E_{form} of *M*N, very well correlates with measured electrical conductivity and extinction coefficient of a–Hf*M*SiBCN. Second, we use *ab–initio* molecular dynamics to model the a–Hf*M*SiBCN materials of experimental compositions and densities themselves. The calculated band gap, localisation of states around the Fermi level and bonding preferences of the *M* element (in particular the tendency of the *M* element to bind with N) also correlate with the measured increasing metallicity with respect to the periodic-table group number of *M*, and confirm the possibility of predicting the trends of characteristics of a–Hf*M*SiBCN using those of *M*N. Third, we study the a–Hf*M*SiBCN properties as a function of each other, and we identify an optimum target composition (B_4C covered by 15% Hf, 5% Ta and 15–20% Si) leading to hard (>20 GPa) films with relatively high conductivity at a given extinction coefficient and vice versa. The results are important for the design of hard, conductive and/or transparent high–temperature coatings.

B5-7 Thermal Stability of Nanostructured TiAl(Si,B)N Coatings Deposited by HiPIMS with Positive Pulses*, **Álvaro Méndez Fernández (alvaro.mendez@nano4energy.eu)**, J. Santiago, I. Fernández-Martínez, A. Wennberg,* Nano4Energy SL, Spain*; M. Panizo-Laiz,* Universidad Politecnica de Madrid, Spain*; M. Monclús, J. Molina-Aldareguia,* IMDEA Materials Institute, Spain

In recent years, due to the advancement of high-speed machining (HSM), more demanding specifications on cutting tool coatings' hardness, chemical inertness materials, wear resistance, anti-abrasion, and also thermal and oxidation resistance are required. In order to overcome the detrimental effects associated with high temperatures during HSM on tool life and workpiece surface finishing, nanostructured coatings based on multilayers or nanocomposites have been proposed [1, 2]. In this work, we present nanostructured TiAlSiN and TiAlBN coatings deposited by HiPIMS with positive pulses. The optimization of the coatings was carried out by tailoring metal ion fluxes and energies. More energetic process conditions have been provided by adjusting height and width of positive pulses. Coatings' microstructure has been studied and related to HiPIMS parameters. The influence of Si and B from 0 to 15% at. content on stabilizing fcc-AlN phase results has also been studied. The formation of nanocrystalline grains (TiAlN) embedded in an amorphous phase (a-Si_3N_4, a-BN) provides enhanced toughness and wear resistance. Hardness up to 40 GPa were measured by nanoindentation techniques and high adhesion critical load values were obtained in nanoscratch testing. High temperature nanoindentation and micropillar splitting were used to evaluate toughness and thermal resistance of the coatings.

[1] J. Musil, Surface and Coatings Technology 125 (2000) 322–330

[2] P. Mayrhofer et al., Progress in Materials Science 51 (2006) 1032–1114

B5-8 Tuning Fracture Characteristics of Superhard Tm Carbide Coatings by Nitrogen Alloying*, **Thomas Glechner (thomas.glechner@tuwien.ac.at)**, R. Hahn,* TU Wien, CDL-SEC, Austria*; D. Primetzhofer,* Uppsala University, Sweden*; H. Zaid, S. Kodambaka,* University of California Los Angeles, USA*; D. Holec,* Montanuniversität Leoben, Austria*; P. Mayrhofer,* TU Wien, Austria*; S. Kolozsvári,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* TU Wien, CDL-SEC, Austria

Cubic transition metal (TM) nitrides and carbides are well-established protective coating materials due to their specific combination of remarkable thermo-mechanical properties but also chemical inertness. Nevertheless, their unique bonding nature – in particular combination of strong covalent and metallic bonds – is also the origin for their lack in fracture tolerance compared to metals and metallic alloys.

To overcome these limitations the formation of carbonitrides by substitutional alloying of the non-metallic sublattice exchanging C with N atoms is an interesting approach. The so obtained adjustment of the valence electron concentration has strong consequences on intrinsic material properties, e.g. Young's modulus, melting temperature, phase decomposition as well as fracture toughness. Therefore, within this study the impact of non-metallic alloying – exchanging C with N atoms – has been explored systematically for two model systems, TaC and HfC, respectively. TM-C thin films were deposited via non-reactive magnetron sputtering, while ternary TM-C-N coatings have been deposited in mixed Ar/N2 atmospheres. We combined ab initio calculations (DFT by VASP) with experimental studies to correlate predicted properties such as fracture tolerance enhancement with increasing VEC (due to nitrogen alloying). The mechanical characteristics have been assessed by micro cantilever bending, pillar compression or splitting tests in correlation to well-established nanoindentation to gain a comprehensive view on the mechanical characteristics – also at elevated temperatures. Furthermore, detailed insights on the phase formation during coating synthesis (also considering influence of structural defects such as vacancies), and hence morphology as well as chemical composition has been studied via ERDA and SEM/HR-TEM, respectively.

B5-9 Improved Ti–Al–Ta–N Coatings by Doping with LaB_6 and $CeSi_2$*, **Alexander Kirnbauer (alexander.kirnbauer@tuwien.ac.at)**, S. Kagerer,* TU Wien, Institute of Materials Science and Technology, Austria*; P. Polcik,* Plansee Composite Materials GmbH, Germany*; P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

The ever-growing need for improved mechanical and thermal resistance of protective coatings ask for their continuous enhancement and optimization. Recently, we showed that $CeSi_2$ or LaB_6 doping (<2 mol%) of well-known and used Ti–Al–N coatings leads to a considerable enhancement of their thermomechanical properties and oxidation resistance. The very positive effects of Ta for Ti–Al–N (with Ta/Ti ratios of ~1/3) are already well documented. Within this study, we further follow the alloying concept by preparing sputtered nitride coatings using $Ti_{0.45}Al_{0.45}Ta_{0.10}$ composite targets alloyed with 2 mol% $CeSi_2$ or 1 mol% $CeSi_2$ plus 1 mol% LaB_6. The thereby developed single-phase face centered cubic LaB_6 and $CeSi_2$ doped Ti–Al–Ta–N coatings outperform the previously studied Ti–Al–Ta–N coatings considerably.

In their as-deposited condition, the LaB_6+$CeSi_2$-doped $Ti_{0.44}Al_{0.42}Ta_{0.13}N$ coatings exhibit a hardness (H) of 37.8±1.5 GPa and an indentation modulus (E) of 498±14 GPa (on polished sapphire substrates). Although the hardness after vacuum-annealing at 1100 °C is with 30.7±1.8 GPa below that of the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$ (39.6±1.3 GPa), the oxidation resistance is simply outstanding. Even after exposure to ambient air at 900 °C for 25 h, the oxide scale thickness is only 800 nm. Thus, easily outperforming the solely LaB_6-doped $Ti_{0.43}Al_{0.57}N$, but also the already excellent oxidation resistance of $Ti_{0.44}Al_{0.44}Ta_{0.12}N$ and $Ti_{0.43}Al_{0.42}Ta_{0.14}Ce_{0.01}N$, which showed 2.4 and 1.9 µm thick oxide scales after 25 h exposure at 900 °C in ambient air, respectively.

Based on our results we can conclude that knowledge-based alloying design is a powerful tool to meet the ever-growing demands of highly-sophisticated applications.

B5-10 Dislocation Confinement in Core-Shell Nanostructures: A Molecular Dynamics Study*, **Drew Fleming (rofleming@astate.edu)**,* Arkansas State University, USA

Recently, a novel nanostructured surface composed of patterned arrays of Al/a-Si core-shell nanostructures (CSNs) has been shown to have a desirable combination of ultra-low friction (COF ~0.015 against a diamond counter face) and high durability. When subjected to instrumented nanoindentation, the individual CSNs show an unusual mechanical response characterized by almost complete deformation recovery, even beyond the elastic limit. Fundamentally, this mechanical behavior is hypothesized to be a result of a back-stress that develops in the confined Al core during compression loading that causes nucleated dislocations to retrace their paths or otherwise annihilate during unloading. In this study, molecular dynamics simulations are utilized to investigate the role that geometry and material properties play on the unique mechanical behavior of CSNs, with special attention paid to the roles of the core material and core-shell interface structure, along with supporting stress calculations.

B5-11 Tribocorrosion Behaviors in Seawater of TiSiCN Coatings Deposited by High Power Impulse Magnetron Sputtering: In-situ Electrochemical Response*, Yixiang Ou (ouyx16@tsinghua.org.cn)*, Beijing Radiation Center, China*; H. Wang,* Beijing Normal University, China*; J. Luo,* Beijing Radiation Center, China*; B. Liao, X. Zhang,* Beijing Normal University, China*; W. Wang,* Beijing Radiation Center, China*; X. Ouyang,* Northwest Nuclear Technology Institute

To meet the requirement and needs of seawater lubrication for mechanical components in marine industry, nanostructured coatings with simultaneously high hardness and toughness are expected to deposit on component surface to enhance working performance and lifetime. Hence, in this work, TiSiCN nanocomposite coatings were deposited on Si (100) and AISI 316L stainless steel wafers by high power impulse magnetron sputtering (HiPIMS) at various peak power of 4-8 kW and negative substrate bias of 0- -200V. Metal Ti and MAX phase Ti_3SiC_2 layers serve as adhesion and transition layers, respectively. Nanocrystalline (*nc*)-(TiN,TiC,TiCN)/amorphous (*a*)-(Si_3N_4, SiC, sp^2-C) nanocomposite structure is obtained in TiSiCN nanocomposite coatings, which exhibits high surface/interface integrity and dense microstructure without distinctly preferred orientation. At 7 kW and -60 V, TiSiCN/ Ti_3SiC_2/Ti coatings with high H, H/E*, H^3/E^{*2} and adhesion exhibit high open circuit potential of -0.07 V, low COF of 0.25 and specific wear rate of $6.1\times10^{-7}mm^3N^{-1}m^{-1}$, resulting from mild abrasive wear without the occurrence of pitting corrosion in 3.5 wt.% NaCl aqueous solution. Moreover, cycling tribocorrosion tests exhibit that passive films possess strong abilities of regeneration and repairation on sliding contact surface thanks to high surface/interface integrity and dense microstructure.

Author Index

Bold page numbers indicate presenter