Hard Coatings and Vapor Deposition Technologies
Room Grand Hall - Session BP

Symposium B Poster Session

BP-1 Electrical and Reliability Characteristics of Dielectric Stack with Low Dielectric Constant SiCOH and Capping SiCNH Films, *C Lee,* National Chi-Nan University, Taiwan*; W Hung,* ***Yi-Lung Cheng****,* National Chi Nan University, Taiwan

The electrical characteristics and reliability of a dielectric stack with a low-k SiOCH film and a capping SiCNH film were investigated in this study. Two different low-k SiOCH films without and with the porosity (called dense and porous low-k) were used to identify the role of the porosity. The deposition of the capping dielectric film on both the dense and porous low-k films increased the overall dielectric constant. A higher increase in the dielectric constant was detected for the porous low-k film due to more serious plasma damage during a capping film deposition. With a capping SiCNH film, O2 plasma damage and Cu diffusion were greatly retarded for both low-k SiOCH films. Lager improvements on TDDB and electromigration lifetimes were detected on the porous low-k film.

BP-3 Adhesion And Durability Of Multi-Interlayered Diamond-Like Carbon Film Deposited On An Aluminum Alloy, ***Hidenobu Maruno****, A Nishimoto,* Kansai University, Japan

Aluminum alloys are light and have good workability; however, they have drawbacks such as low hardness and poor wear resistance. These drawbacks limit their wide application in the automotive field. The deposition of a diamond-like carbon (DLC) film, which has high hardness and good wear resistance, on the substrate surface can improve these drawbacks. Because aluminum alloys and DLC films have poor affinity, the adhesion between them is poor. However, the usage of an interlayer can improve the adhesion between them. In this study, to investigate the effect of multi-interlayers on the adhesion and durability, a DLC film with an interlayer of Ti, Si-DLC, or Ti/Si-DLC was deposited on the EN AW-2024 Al alloy substrate via plasma enhanced chemical vapor deposition. Argon bombardment treatment was conducted to clean the substrate surface before deposition, the Ti interlayer was deposited via sputtering for 15 min, the Si-DLC interlayer was deposited using gas mixture of tetramethylsilane and methane for 15 min, and DLC was deposited using methane gas for 90 min. The nano-hardness of the Ti/Si-DLC multi-interlayered sample reached 21 GPa, which is nearly 4 GPa more when compared with single interlayered samples. A ball-on-disc test showed that the wear volumes of the ball and the multi-interlayered sample were smaller compared with the single interlayered samples. In addition, the durability distance of the Ti/Si-DLC multi-interlayered sample was 3300 m, increasing more than 1500 m than the single interlayered samples.

BP-4 The Effect of Cu on Fatigue Properties of TiZrNbN Coatings, *H Aghdam, A Keles,* Ataturk University, Turkey*; O Baran,* Erzincan University, Turkey*; Y Totik,* Atatürk University, Turkey*;* ***Ihsan Efeoglu****,* Ataturk University, Turkey

The fatigue properties are very important for cutting tools due to service life. Due to improve fatigue properties of cutting tools, transition metal nitrides with soft metal (Cu, Ni etc.) are coated on cutting tool materials. To investigate Cu effect on fatigue properties of transition metal nitride coatings, TiZrNbN and Cu doped TiZrNbN coatings were deposited on M2 high speed steel using reactive closed field unbalanced magnetron sputtering (CFUBMS) in bias voltage of -80V, coating pressure of 0.26 Pa and Cu target current of 0.6 A. Microstructure properties of the coatings were determined by XRD, SEM and EDAX. Mechanical properties of the coatings were examined with microhardness test. Fatigue properties of the films were examined using multipass scratch tester. According to the results, the mechanical properties of TiZrNbN doped Cu is better than TiZrNbN.

BP-5 Thermal Stability of Ni-B/ La_2O_3 Coatings by Electro-brush Plating Technique, ***Dan Zhang****, X Cui, G Jin, Z Cai, M Dong,* Harbin Engineering University, China

The metastable materials have gained a great deal of attraction due to their promising physicochemical properties, but the thermal stability limits their practical application. In this paper, Ni-B/La_2O_3 amorphous/nanocrystalline composite coatings were prepared on AISI 1045 steel substrate by electro-brush plating technique. The surface morphology, component and the phase structure of coatings were observed by Scanning Electron Microscope (SEM), Energy Dispersive X-Ray Spectroscopy (EDS) and X-Ray Diffraction (XRD), respectively. The coatings were further analysis by Transmission Electron Microscope (TEM). Then the thermal stabilities of coatings with different content of La_2O_3 were also analyzed under different annealing temperature. It was found that the coating had a unique microstructure consisting of amorphous and nanocrystalline structures. The addition of La_2O_3 does improve the thermal stability of metastable Ni-B coatings when the annealing temperature is over 355℃. In addition, the thermal stability of the amorphous/nanocrystalline coatings depends on the percentage of amorphous phase, grain sizes and textures.

Acknowledgements

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BP-6 Properties of CrN_x Thin Films Deposited in Plasma Activated Polymers by Reactive Magnetron Sputtering, *M Rodrigues, P Pedrosa,* Minho University, Portugal*; A Ferreira, L Godinho, M Amaral,* PRIREV, Portugal*; M Neto, F Oliveira, R Silva,* Universidade de Aveiro, Portugal*; J Borges,* ***Filipe Vaz****,* Minho University, Portugal

Polymers are replacing traditional metallic materials, particularly in the automobile, electronic and decorative industries. Their low density, flexibility, design versatility and low cost production, combined with the properties of a shining, highly reflective and conductive metallic coating, gives them a huge advantage over common metals. One of the most used metallization process in the last decades has been chrome plating using highly toxic hexavalent chromium. However, following all the enacted legislation during the last years against the use of hexavalent chromium solutions, new chrome plating alternatives have emerged and include chemical, physical, and mixed approaches. One of such techniques is magnetron sputtering, which can be used on a wide range of available polymers and has a reduced environmental impact, unlike chrome plating.

In this work, magnetron sputtered CrN_x thin films were deposited on several polymers, including ABS, PA and PP. Two sets of thin films were obtained by varying the N_2 flow inside the vacuum chamber (series 1) and the deposition time (series 2). The polymers where also subjected to plasma treatment in Ar prior to the CrN_x thin films' deposition in order to enhance the adhesion. The fundamental microstructural, chemical and physical properties, as well as the quality and adhesion of the CrN_x thin films, were accessed by SEM, XRD, 3D profilometry, colorimetry, electrical resistivity measurements and scratch test. Main results show that high-quality, dense CrN_x films with enhanced adhesion and low percentage of defects were obtained. Magnetron sputtering is thus a promising alternative to the hazardous chrome plating for an effective metallization of different polymers.

BP-9 Influence of Ti on the Phase Stability of Magnetron Sputtered Mo-Si-B Thin Films, ***Elias Aschauer****, H Riedl,* CDL-AOS at TU Wien, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

In terms of fuel and cost efficiency, the replacement of high-density Ni-based super alloys in aerospace industries came into the focus of research. A promising candidate are Mo-Si-B alloys, since they offer a high creep resistance, phase stability in a very broad range as well as excellent oxidation resistant. This broad field of mechanical and chemical properties is achieved by taking advantage of different phase combinations within the ternary phase diagram, leading to a multicomponent material. As it is well known in literature, molybdenum offers a poor oxidation resistance due to the formation of volatile oxides already above 400 °C – so called pesting phenomena. Alloying silicon and boron to refractory metals like molybdenum promotes the formation of glassy-like borosilicate oxide scales and inhibits the volatilisation of MoO_3. Nevertheless, retarded oxidation kinetics in a wide temperature field is strongly linked to the proper Si to B ratio. The molybdenum rich corner, known as Berczik triangle, offers a phase combination of Mo (A2), c-Mo_3Si (A15), and T_2–Mo_5SiB_2 ($D8_l$), next to the so-called Akinc triangle including c-Mo_3Si (A15), T_2–Mo_5SiB_2 ($D8_l$), as well as T_1-Mo_5Si_3 ($D8_m$). Especially, the T_1 and T_2 phases provide the ideal ratio of boron and silica to form either B-rich SiO_2 or even pure SiO_2 at low and high temperatures, respectively.

In order to access this highly interesting material characteristics, physical vapour deposition (PVD) can be used to make this promising material system accessible to many other applications and extend the field of operation. However, the most common deposition temperatures of about 500 °C do not lead to the desired phase combination, but rather to

homogeneous, X-ray amorphous thin films. Alloying titanium to the ternary system is known to stabilise the T_2 phase, by substituting the Mo atoms within the tetragonal crystal structure up to concentrations of 40 % - also reducing the density significantly.

Therefore, the focus of the provided study is on the fundamental understanding of the phase evolution of magnetron sputtered Mo–Ti-Si–B thin films varying deposition parameters such as total pressure, bias voltage, and deposition temperature. Furthermore, the phase stability after thermal treatments in different atmospheres (vacuum, inert gas, and oxygen) is investigated up to temperatures of

1500 °C by using X-ray diffraction analysis as well as various (high-resolution) electron microscopy techniques and differential scanning calorimetry (DSC). The mechanical properties were investigated by nano-indentation of the as deposited and annealed state.

BP-10 Carbide Layer Coating on Titanium by Spark Plasma Sintering Technique, ***Akio Nishimoto***, *C Nishi,* Kansai University, Japan

Titanium materials are widely used in aerospace, automotive and biomaterial engineering fields due to high specific strength, superior fatigue and corrosion resistance as well as excellent biocompatibility. However, titanium exhibits low hardness and poor wear resistance. Therefore, the development of a suitable surface modification technology is necessary to expand the use of titanium materials. In order to improve hardness and wear resistance of materials, there is the method to form the hard ceramics layer on the matrix surface. In this study, carburizing method was applied. The carburizing method can form the carbide layer which is superior in adhesion with the matrix compared with PVD or CVD method. However, in conventional carburizing methods, the deterioration of the mechanical properties of the matrix as a result of long-term and high-temperature processing is problematic. Therefore, spark plasma sintering technique, which features short processing times, was applied to form a carbide layer in this study. The purpose of this research is to form a TiC layer on commercially pure Ti (CP-Ti) and evaluate its properties. CP-Ti was used as the substrate, and graphite powder was used as the carburizing source. XRD analyses indicated that a TiC layer was formed on the substrates. Corrosion tests indicated that the corrosion resistance of the carburized samples was remarkably improved compared to that of CP-Ti. Wear tests revealed that the carburized samples exhibited low friction coefficients and improved tribological properties.

BP-13 Growth Kinetics of Boride Coatings on AISI W2 Steel, ***MarcoAntonio Doñu Ruiz***, Universidad Politécnica del Valle de Mexico, Mexico*; N Lopez Perrusquia,* Universidad Politecnica Del Valle De Mexico, Mexico*; V Serna Lara, V Cortés Suárez,* Universidad Politécnica del Valle de Mexico, Mexico

The present work evaluate the growth of the boride coatings formed in the surface AISI W2 steel by powder pack boriding. This process was carried out in the temperature range of 1173–1273 K with the exposure times ranging from 2 h to 8 h. The presence of borides Fe_2B formed on the surface of steel substrate was confirmed by optical microscopy and X-ray diffraction. The distribution of alloy elements from the surface to the interior was confirmed by energy dispersive X-ray spectroscopy.

The morphology presented the boride layer Fe_2B showed smooth and compact, with range thickness average from 9.96 ± 2.61 µm to 45.86 ± 4.13 µm. A mathematical model of the growth kinetics of the Fe_2B coatings on AISI W2 was proposed for the powder-pack boriding. The boron diffusion coefficient (D_{Fe2B}) was determinated by mass balance equation of the (Fe_2B/substrate) interface, the kinetic model was set for the Fe_2B coatings, assuming that the growth of boride layers follows a parabolic growth law. In addition, a contour diagram describing the evolution of Fe_2B coatings as a function of time and temperature parameters was proposed to be used in practical application. Finally, the boron activation energy for the AISI W2 steel is estimated as 183.44 kJ mol^{-1} and this value of energy was compared with the literature data.

BP-15 Study on Steels Boronizing Immersed in Diesel, ***Noe Lopez Perrusquia***, *M Doñu Ruiz, G Perez Mendoza,* Universidad Politecnica Del Valle De Mexico, Mexico*; V Cortés Suárez,* Universidad Autónoma Metropolitana- Azcapotzalco, Mexico*; C Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico

This work shows the effect of diesel on a surface coating of boron in Microalloyed Steels. The steels are boronizing at 1273 K, with permanence of 6 h; the medium boriding by boron paste dehydrated; the medium boriding by boron paste dehydrated in solid box; the immersion of the steels Microalloyed boriding for 1 year in diesel at temperature ambient. The first phase consisted in the characterization and analysis of FeB/Fe_2B obtained by paste dehydrated of boron, using optical microscopy (OM), scanning electron microscopy (SEM), energy dispersive spectrometry (EDS), X-ray diffraction (XRD) and microhardness (Hv). The second phase is the immersion of the boriding specimens in diesel, after the permanence time, were evaluated by the tensile test and analyzed the mechanical properties. This work presents the formation of boron coating, with the purpose of showing an alternative for the manufacturing industries; which generate containers for storage of liquids, biofuels and fuels

BP-17 Deposition of Nanodiamond Coatings on Steel Implant Materials with CrN/Al Interlayer, *Y Li, F Ye, C Zhang, M Taheri, J Corona,* ***Qiaoqin Yang***, University of Saskatchewan, Canada

Integration of smooth nanocrystalline diamond coatings on steel substrates for biomedical implant applications has great application potentials due to their extraordinary wear/corrosion resistance and biocompatibility. However, CVD deposition of adherent and continuous diamond coating on steel substrates has met technical barrier of easy delamination. We will report on our recent progress on enhancing the adhesion of diamond coatings on steel substrates by using CrN/Al interlayer. The morphology, microstructure, composition and adhesion of the formed surface products are comprehensively characterized by SEM, TEM, XRD, Raman and synchrotron XAS as well as indention test. The fundamental mechanism of enhanced interfacial adhesion is discussed.

BP-18 MoN/TaN Superlattices: from a Computer Design to a Realization, *N Koutna,* TU Wien, Institute of Materials Science and Technology, Austria*; R Hahn,* CDL-AOS at TU Wien, Austria*; J Zalesak,* Montanuniversität Leoben, Austria*; M Friak,* IPM, Academy of Science, Czech Republic*; M Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria*; M Sob,* Masaryk University, Czech Republic*; J Keckes,* Montanuniversität Leoben, Austria*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria*;* ***David Holec***, Montanuniversität Leoben, Austria

Nitrides are fascinating class of materials constantly revealing new and unexpected features, often related to metastable phases accessible via, e.g., non-equilibrium physical vapour depositions. Cubic MoN and TaN have been recently shown to strongly favour vacancies.

First principles calculations of undefected MoN/TaN superlattices suggest an interface-induced structural transformation from cubic to tetragonal phases (ζ-TaN, ζ-MoN). An analysis of their elastic constants reveals that the TaN volume fraction must be larger that that of MoN in order to be mechanically stable. This stability range can be further influenced by considering the point defects, namely vacancies. It is shown that the stability of superlattices critically depends not only on the amount of vacancies, but also on their distribution as well as on the superlattice bi-layer period. Impact of the interface and its orientation on the tensile strength is also briefly presented.

To compare the calculated results with experiments, magnetron-sputter deposited superlattices with various bi-layer periods are studied using conventional XRD, conventional and high-resolution TEM, and mechanical testing. The structural analysis confirms single-phase cubic superlattices with a strong (100), (110) or (111) interface orientation, as dictated by the MgO substrate orientation. Quantitative EELS measurements are used to prove the non-stoichiometry of individual constituents, MoN and TaN, as a function of the bi-layer period.

BP-20 Effect of Mo Concentration on Structure and Properties of Zr-Mo-N Thin Films Deposited by Reactive Magnetron Sputtering, *A Junior,* ***Daniel Fernandez***, *L Félix,* Universidade Federal de Sergipe, Brazil*; R Hubler,* Pontifícia Universidade Católica do Rio Grande do Sul, Brazil*; F Mendes,* Instituto Nacional de Tecnologia, Brazil*; G Brito,* Universidade Federal de Sergipe, Brazil*; E Tentardini,* Universidade Federal de Sergipe, Brazil, Brasil

Zirconium nitride (ZrN) thin films are mentioned in many studies because of their excellent characteristics that allow their application in cutting and molding tools. However, the columnar growth, micro cracks and porosity of that material compromise its mechanical properties and limit its oxidation resistance. One of the alternatives to solve that problem is the addition of a third element to its matrix. Some studies show that molybdenum addition result in expressive improvements in mechanical properties and wear resistance, as in TiMoN and CrMoN, however there are few works about the effect of Mo in ZrN coatings properties. The objective of this work is to study the influence of molybdenum on the structure, morphology, mechanical properties and oxidation resistance of zirconium and molybdenum thin films (ZrMoN). Thus, thin films of the system ZrMoN were deposited using reactive magnetron sputtering (RMS) technique, varying the molybdenum content in 23, 31 and 37 at.%. Thin films were

characterized by GAXRD, SEM, XPS and high temperature oxidation tests at three different temperatures, 773K. 873K and 973K. GAXRD analysis showed a molybdenum accommodation in the lattice forming substitutional type solid crystalline solution and a small displacement of the ZrN peaks to the right as theMo content rises. Sample with 23 at% of Mo into structure reach 33 GPa, the highest value for all coatings studied. All samples failed in oxidation tests, with reduction of hardness values; appearance of bubbles and loss of adhesion.

BP-21 Anti-staining Coatings on PET Fabrics by Using a Spraying/ Plasma-Polymerization Duplex Technique, ***Cheng-Wei Lin,*** Feng Chia University; Central Taiwan University of Science and Technology, Taiwan*; J He,* Feng Chia University, Taiwan

To fulfill better wearing quality, PET fabrics are considered for further treatment to resist environmental dust and oil stains. This study aims to prepare a hydrophobic surface on PET fabrics to minimize the risk of dust adhesions or oil stains by using a duplex technique combining spraying and low-surface-energy plasma polymerization. The anti-staining coated fabrics are tested their durability by using the AATCC 130 of washing test for barbecue sauce and ketchup.

Experimental results reveal that the duplex treated fabrics can achieve water contact angle (WCA) over 118°. Anti-staining tests performed at 1, 4, and 10 weeks after surface treatment show that the the tested fabrics can tolerate 10 times of the washing test without altering surface appearance. Results of SEM and EDS analysis show that fluorocarbons still exhibit on the surfaces of PET fabrics after anti-staining tests. Above all, a spraying/plasma polymerization duplex coating on the surfaces of PET fabrics exhibits favorable hydrophobicity and anti-staining durability.

BP-22 Fracture Resistance of Nanocomposite/Metal Nitride Multilayers: Role of Interfaces, ***Naureen Ghafoor***, *P Persson,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; I Petrov,* Linköping University, IFM, Thin Film Physics Division, Sweden, USA*; J Barriero, F Mücklch,* Saarland University and Materials Engineering Center Saarland, Germany*; J Birch,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; W Clegg,* Cambridge University, UK

The focus is deformation mechanisms of transition metal nitride nano-composites coatings. The deformation in these materials is strongly dependent on interface structure and become more complex in nano-composites involving high density of interfaces. We present mechanical response of TiN/ZrAlN multilayers and monolithic ZrAlN nano-composite coatings investigated through nano indentation and micropillar compression tests. The study highlights effect of interface structure on pre yield and post yield behavior of nano scale multilayer deformation in compression.

To understand stress-strain response in a uniaxial micropillar compression tests the pillars of height of 1 mm and diameter of 300 nm were compressed using in situ SEM nanoindenter equipped with a flat punch (diameter 5mm)[Ref 2]. The pillars were milled using focused ion beam. The interface structure of the multilayers is tuned by varying growth parameters during magnetron sputter deposition on MgO (001) substrates. The growth temperatures above 700 °C facilitated in situ segregation of ZrN-and AlN- rich domains within ZrAlN layer during growth [Ref 1]. The growth conditions and multilayer design are varied to tailor crystal structure of AlN rich domains from cubic to wurtzite and consequently to obtain coherent, semicoherent, and incoherent interfaces. Dependence of plastic deformation and work hardening on the multilayer period as well as on the coherency of involved interfaces is investigated. Micropillar compression tests revealed higher yield stresses and larger post yield displacements in 2 and 5 nm thin ZrAlN layers consisting of cubic phases of ZrN and AlN- rich domains forming coherent interfaces. For 15 and 30 nm thick ZrAlN layers, involving incoherent interfaces, the dominant crack propagation occur through layer interfaces. The dominant deformation mechanisms in connection with interface coherency and multilayer periodicity will be presented.

BP-23 Vacancies in Al-O-N Crystallites, ***Maria Fischer***, *D Scopece, C Pignedoli, D Passerone, H Hug,* Empa, Swiss Federal Laboratories for Materials Science and Technology, Switzerland

Aluminum oxynitride (Al-O-N) in its transparent ceramic form provides attractive properties for hard coatings. Thin films of this material with different O and N contents were deposited by reactive unbalanced closed field direct current magnetron sputtering (R-UCFDCMS) and investigated with respect to the induced changes upon varying O/N ratios.

It was discovered that O addition leads to a gradual transformation of polycrystalline wurtzite AlN via Al-O-N nanocomposite towards amorphous Al_2O_3. The boundary between polycrystalline AlN and Al-O-N nanocomposite is set by the solubility limit of O in AlN and was found to be at 8 at% O. Below this critical value, O substitutes N in in the wurtzite lattice. This leads to a continuous unit cell shrinkage in c direction measurable by XRD. Above 8 at%, O starts to surround crystallites in the form of an amorphous Al_2O_3 matrix.

The shrinkage of the c lattice parameter upon O incorporation can hypothetically be attributed to the generation of Al vacancies. Since O has one valence electron more than the N it replaces, the ideal wurtzite 1:1 stoichiometry of electron donor and acceptor as found in AlN can no more be matched. In order to maintain the wurtzite crystal structure, the proportional amount of Al has to reduce to fit the stoichiometry $AlO_{1.5x}N_{1-x}$. The hypothesis that this is achieved through vacancies in the Al lattice positions was tested by ab initio DFT calculations. Lattice parameter changes upon O introduction and consequent Al vacancy defect generation were calculated and found to be in good agreement with the experimentally observed values. The obtained results were compared to data for the related ternary Al-Si-N system.

BP-26 Effects of Bias Voltage on Microstructure and Properties of Al-doped Hydrogenated Amorphous Carbon Films Prepared by a Hybrid Deposition Technique, ***Songsheng Lin,*** *W Xu, H Li, M Dai, Q Shi, C Wei, H Wang, K Zhou,* Guangdong Research Institution of New Materials, China

Al-doped hydrogenated amorphous carbon films were deposited on Si wafers and stainless substrates by a hybrid deposition technique composed of middle-frequency magnetron sputtering and anode layer ion source. Effects of substrate bias voltage on the deposition rate, surface topography, microstructure, residual stresses and mechanical properties were characterized using scanning electron microscope (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and nano-indentation. It was shown that the aluminum atoms were embedded in carbon matrix without bonding with C atoms. The surface of the films evolved from a rough surface with quasi-columnar characteristic to a smoother surface with the applied bias voltage increased from 0 to -400V. The residual stresses of the films deposited at 0V and -50Vwere tensile stress, while it transformed to compressive stress with bias voltage increased to -100V or higher. The hardness of the film stayed in the highest level of nearly 17GPa, while the bias voltage ranging from -150 to -300V. The ball-on-disk tribo-meter was further used to study the tribological behavior, the results demonstrated that the film deposited at -150V exhibited excellent lubrication performance with a fiction coefficient of about 0.047 and good wear resistance.

BP-27 Comparison of Chromium Carbide Thin Films Grown by Different Power Supply Systems, *Z Li, C Wang,* National Taiwan University of Science and Technology, Taiwan*; B Lou,* Chang Gung University, Taiwan*;* ***Jyh-Wei Lee,*** Ming Chi University of Technology, Taiwan

The potential use of chromium carbide thin films has been a great interest to academia and industry due to their outstanding properties such as chemical stability, low coefficient of friction, adequate hardness and high wear resistance. In this study, the chromium carbide thin films were fabricated by a magnetron sputtering using different power supply systems, including direct-current (DC), high power impulse magnetron sputtering (HiPIMS), and superimposed middle-frequency (MF)-HiPIMS. The Cr target poisoning status was controlled by a plasma emission monitoring system by adjusting the gas flow ratio of Ar and acetylene (C_2H_2). The morphology and microstructure of thin films were evaluated by scanning electron microscope. The crystallinity of films was studied using X-ray diffractometer. The electron probe micro analyzer, X-ray photoelectron spectroscope, and Raman spectroscope were used to determine the chemical compositions and binding structures of thin films. The mechanical, adhesion and tribological properties were explored by using scratch tester, tribometer, and nanoindentation. The influence of different power supply systems on the microstructure, chemical composition, and mechanical properties of chromium carbide films were investigated in this work.

BP-28 Self-organized Formation of Different Nanostructure in Carbon-metal Films Prepared by Reactive Magnetron Sputtering, ***Hongxuan Li***, *W Wang, L Ji,* Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China

Metal-containing carbon-based films (Me-C films) have been attracted much attention because metal-dopping can effectively improve and regulate film's properties (such as reducing the internal stresses, enhancing

the adhesion to the substrate and improving environmental sensitivity of tribology). It has been wildly reported that various metals have been introduced into carbon-based films by different groups. However, it will bring wide differences in precisely controlling microstructure and interaction mechanism etc. aspects to metallic dopping carbon-based films due to diverse metallic elemental, prepared methods and conditions.

This report highlights a peculiar phenomenon that spontaneous formation of various nanostructure in the carbon-based films during co-deposition of different metallic element process. Consideration of different interaction between metal and carbon, we choice copper, titanium, and nickel as three typically dopping metals. The influence of various metallic elements on self-organizing special nanostructure in carbon-metal films is systematically studied. For copper, it is noncarbide and immiscible with carbon, self-organized nano-multilayered structure can be formed in the copper-carbon film when the copper concentration maintaining at 20%-40% at.%; Titanium are strong carbide former, the nanocomposite structure of titanium carbide nanocrystalline dissolved in the amorphous carbon matrix is observed in the titanium-carbon film; Nickel possess the ability to catalysis the growth of carbon nanowires, and self-organized carbon nano-wires structure in nickel-carbon film has been successfully prepared, the field-emission tests of this self-assembled carbon nanowires structured film shows excellent behaviors.

BP-29 Anticorrosive Properties of (Zr-Si-Ti-N)Ni Thin Films Deposited by Co-Sputtering, ***EstrellaNatali Borja Goyeneche***, *J Olaya,* Universidad Nacional De Colombia, Colombia

In the present work, the influence of nickel content on the structural and electrochemical properties of the TiZrSiN films was investigated. The nanostructured ZrSiTiN thin films with nickel additions were deposited onto stainless steel AISI 316L and TiAlV alloy substrates using the reactive magnetron co-sputtering technique. The structure was analyzed by X-ray diffraction and the chemical composition was identified by energy dispersive X-ray spectroscopy (EDS). The corrosion resistance was studied by potentiodynamic polarization test and electrochemical impedance spectroscopy using a 3.5 wt% NaCl corrosive solution. Nickel leads to improve the anticorrosive properties of thin composite films because to the incorporation of a physical barriers against the propagation of the corrosive electrolyte. The corrosive mechanism is discussed in this paper.

BP-30 Corrosion Resistance of Stainless Steel Coatings With and Without Silver Deposited by Sputtering, ***ClaudiaLiliana España***, *J Olaya,* Universidad Nacional De Colombia, Colombia; *A Candido Recco,* Universidade do Estado de Santa Catarina, Brazil

The anticorrosive properties of stainless steel coatings deposited with different amounts of silver by unbalanced magnetron sputtering were studied. The structure of the coatings were characterized by means of X-ray diffraction, the morphology and chemical composition were evaluated by means of scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) respectively. The corrosion resistance was determined through out of potentiodynamic polarization tests and electrochemical impedance spectroscopy using a Ringer's solution as a simulated biological fluid. It was determined that the coatings deposited in inert atmosphere presented BCC structure, while the coatings deposited in the reactive atmosphere shows the BCC and FCC phases. A compact morphology was observed in coatings with a higher silver content. The corrosion resistance was increased in the coated substrate compared to the uncoated substrate. Corrosion mechanism of coating deposited is disscused in this paper.

BP-31 Evolution of Structure and Mechanical Properties of Nanocrystalline Multi-layered Arc-evaporated AlCrN-AlTiN Coatings upon Thermal Loading Revealed by X-ray Nanodiffraction and Tribological Testing, ***Stefan Klima***, *N Jäger, M Meindlhumer,* Montanuniversität Leoben, Austria; *H Hruby,* eifeler-Vacotec GmbH, Germany; *J Keckes, R Daniel,* Montanuniversität Leoben, Austria

Nanocrystalline coatings are typically characterized by inherent variations in the structure (texture and size of grains), residual stress and mechanical properties over the thickness, which is associated with the competitive nature of their growth. On the other hand, the microstructure and thus the coating properties may be intentionally controlled by a specific multilayer architecture, in which crystallographic structure, size of grains as well as the stress state may be influenced by layer thickness and templating effects. In order to understand the complex structure-stress-property variations in hierarchical nanostructured coatings, a multi-layered multi-phase arc-evaporated AlMeN-based coating system (where Me=Cr and Ti) was developed and studied by cross-sectional position-resolved synchrotron X-ray nanodiffraction and tribological testing in the as-deposited state and after thermal treatment. Since both AlMeN systems are metastable transition metal nitrides having either cubic or hexagonal crystallographic structure depending on the Al-content, their phase composition was controlled either by the cathode composition or deposition conditions. Furthermore, potential (de)stabilization of the crystallographic structure of the metastable constituents was studied in detail for the multi-layered system, where AlCrN and AlTiN sublayers prepared at bias voltages ranging between -30 and -600 V alternated with layer thicknesses varying from 10 to 300 nm. The X-ray nanodiffraction analysis revealed that the cubic structure of the AlMeN layers may be stabilized even at high temperatures while combed with cubic sublayers in a multilayer structure, although they otherwise exhibit a dual phase structure as monolithic coatings. The role of the coating architecture on the structural stability and the stress state will be demonstrated for a number of multilayer design variations.Furthermore, coatings with a specific architecture were selected based on the results of the cross-sectional combinatorial approach and tested by pin-on-disk experiments at RT and 600 °C. The results document strong relationships between the architecture, phase composition, stress state, thermal stability and wear resistance of the coatings, which allow to establish specific design rules for thermally and mechanically stable multi-layered AlN-based coatings.

BP-32 Corrosive Resistance of Nanostructured ZrSiN-Ag Films Deposited by Reactive Sputtering, *H Vanegas Parra,* ***JhonJairo Olaya***, *J Alfonso,* Universidad Nacional De Colombia, Colombia; *S Calderon,* International Iberian Nanotechnology Laboratory, Portugal; *S Carvalho,* University of Minho, Portugal

Due to their physical and chemical properties the multifunctional materials have been study extensively in the last years. In this work we present the growth of nanostructured ZrSiN-Ag films deposited on common silicon and stainless steel substrates via magnetron co-sputtering with aim of analyze the influence of silver amount on the crystalline structure and corrosive resistance. The coatings structure have been characterized through X-ray diffraction (XRD) and the morphology has been evaluated via scanning electronic microscopy (SEM); anticorrosive properties were carried out through potenciodinamic polarization test. The preliminary results, shows that the films are polycrystalline and the corrosion resistance improve as a function of the Si and Ag amount in the films deposited. The corrosion mechanism in the films will be discussed in this work.

BP-33 Mechanical Properties of ZrSiN-Ag Thin Films Deposited by Reactive Magnetron Sputtering, ***HenrySamir Vanegas Parra***, *J Alfonso, J Olaya,* Universidad Nacional De Colombia, Colombia; *S Calderon,* International Iberian Nanotechnology Laboratory, Portugal; *S Carvalho,* University of Minho, Portugal

ZrSiN-Ag thin films were deposited by reactive magnetron sputtering in order to study the effect of addiction of silver on the structure, chemical composition and mechanical properties in ZrSiN thin films. The structure of thin films was characterized by X-ray diffraction (XRD), the morphology by scanning electron microscopy (SEM) and the chemical composition by energy-dispersive x-ray spectroscopy (EDS). A nanoindenter was used to study the mechanical properties such as hardness and elastic module in function the silver content in the films deposited. The XRD results showed that nanostructured ZrSiN-Ag thin films were obtained. The ZrN film exhibited a face-centered cubic (f.c.c) phase with columnar structure while that the Zr-Si-N films showed a mixture of f.c.c and near-amorphous phases without columnar structure, similar to the ZrSiN-Ag films. The hardness obtained for ZrN film was of 58,80 GPa, which decreases as silver contents increase.

BP-34 Hardness and Adhesion of AlSiN Thin Films Deposited by the Simultaneous Laser Ablation of Two Targets, ***Enrique Camps***, *L Rivera, I Campos-Silva,* Instituto Nacional de Investigaciones Nucleares, Mexico; *S Muhl,* Universidad Nacional Autonoma de Mexico, Mexico

Aluminum silicon nitride (AlSiN) thin films with different Si content were deposited using the simultaneous laser ablation of aluminum and silicon targets in a nitrogen atmosphere and a substrate temperature of 200 °C. Films were deposited at two values of working pressure, 0.6 and 1 Pa. The silicon content in the films ranged between 3 and 20 at. %, and was varied by changing the density of the plasma produced during the ablation of the silicon target, i.e. the highest the plasma density gave the highest the silicon concentration in the films. The plasma parameters (mean kinetic ion energy and plasma density) were measured using a planar Langmuir probe. Samples deposited with low silicon contents (up to about 6 at. %), contained nanocrystals embedded in an amorphous matrix. Those crystals

were identified as hexagonal aluminum nitride (w-AlN). For higher concentrations of silicon the amorphous phase was predominant and the nanocrystals were no longer observed. The hardness of the films had a maximum value of 30 Gpa, and an elastic recovery of about 50 % when the silicon content was close to 4 at. %. For higher silicon concentrations the hardness was lower at 19 GPa. Scratch tests were carried out on samples with different silicon contents. For the samples with low silicon contents (the highest hardness) delamination was observed at loads of 90 N, in the transition to the solid solution regime (Si content of 8 at. %) delamination was observed to begin at 10 N, and for the highest concentrations of silicon no delamination of the films was observed even for loads of 90 N.

BP-35 Plasma Enhanced Chemical Vapor Deposition of Carbon Film into a Small Hole 100 µm in Diameter with MVP and Source Gas Blowing, *R Ota,* Nagoya University, Japan*; **Hiroyuki Kousaka**,* Gifu University, Japan*; L Raja,* University of Texas at Austin, USA*; N Umehara, M Murashima, T Tokoroyama,* Nagoya University, Japan

Diamond-like carbon (DLC) is widely applied to mechanical parts because of its low friction performance, high wear and corrosion resistance. When it is applied to the internal surface of a hole, plasma enhanced chemical vapor deposition (PECVD) is typically used because of its excellent coating coverage to 3-dimensional internal surfaces. However, it is not feasible to generate plasma in an 100's-µm-diameter hole due to the formation of ion sheath whose width is comparable to the inner diameter. In this case, the precursor molecules of DLC such as CH_3 radical are transported by diffusion into the inside of a hole from plasma generated at the outside. However, the radical density decreases exponentially in axial direction by sticking loss to the internal surface of a hole. Consequently, the depth of the internal surface covered by DLC (referred to as coating depth) has no choice but to become almost the same as its diameter [1]. Since the aspect ratio of a hole in mechanical parts is typically more than 10 (e.g. fuel injector), it is strongly required to increase coating depth. Thus, in this research, we propose the novel coating method by PECVD coupled with source gas blowing to increase coating depth for an 100-µm-diameter hole. Particularly, We investigate the effect of blowing source gas and flow rate on the coating depth of DLC.

In order to deposit DLC to the inner surface of a small hole 0.1 mm in diameter and 5 mm in depth, PECVD employing MVP is conducted with blowing source gas from nozzle to the hole inlet. After DLC coating, film thickness is measured by 0.1 mm in axial direction of the hole and the maximum depth where a film thickness is detectable is defined as coating depth. We found that blowing source gases increases coating depth. Furthermore, the linear increase of coating depth from 0 to 1 mm was observed with the increase of the flow rate of blown gas from 0 to 780 sccm. We are going to further investigate the effect of source gas flux on coating depth by numerical simulation of plasma with the commercial software VizGlow at the conference.

References

[1] R. Ota, H. Kousaka, L L. Raja, N. Umehara, M. Murashima: Internal DLC Coating to Small Hole in a Diameter of 100 µm by Plasma Enhanced Chemical Vapor Deposition with Gas Blowing to the Hole, ICMDT 2017, (2017).

BP-37 Effect of Silicon Content on Structure and Properties of AlCrSiN Coatings Prepared by Arc Ion Plating for Milling Tools, ***Wangryeol Kim***, *S Heo,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; Y Kim, J Kim,* KORLOY, Republic of Korea*; I Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Quaternary AlCrSiN coatings with silicon content ranging from 0 to 21 at.% were deposited on WC-Co alloy substrates by an arc ion plating technique using Cr-Al and Cr-Si composite targets in an N2/(Ar+N2) gas m ixture for hard material processing milling tools. The microstructure, mechanical, wear, tribological properties of the coatings were investigated by XRD, XPS, FESEM, HRTEM, surface 3D profiler, nano-indentation, scratch tester, and ball-on-disc tribo-meter. As the silicon content increased, the microstructure of the coatings changed from columnar grains to interconnected fine grains, and finally to nanocomposite structure, in which (Al,Cr)N nanocrystallites were surrounded by an amorphous silicon nitride matrix. The incorporation of silicon results in the (Al,Cr)N crystallite size refinement and the decrease of the average surface roughness. The nanohardness of the AlCrSiN coatings showed higher hardness values than that of AlCrN coating. The strengthening mechanisms include solid solution hardening and grain boundaries strengthening through the formation of a thin amorphous layer. Moreover, it was found that the improved nanohardness and the H/E ratio contributed to excellent wear resistance of the coatings. The friction coefficient and wear rate of the AlCrSiN coatings first decreased and then increased with increasing silicon content. The friction coefficient and wear rate were also mainly related to the lubricant wear debris in this work.

BP-38 Coatings and Performance Evaluation of Ti–Al–Si–N–O Coated Cutting Tools, ***Sungbo Heo***, *H Kim, U Jung,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; Y Kim, J Kim,* KORLOY, Republic of Korea*; I Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Functional graded Ti–Al–Si–N–O nanocomposite coatings were deposited onto WC-Co substrates by a filtered arc ion plating system using $TiAl_3$ and Ti_4Si composite targets under N2 atmosphere. XRD and XPS analyses revealed that the synthesized Ti–Al–Si–N–O coatings were nanocomposite consisting of nanosized (Ti,Al,Si)N crystallites embedded in an amorphous Si_3N_4/SiO_2 matrix. The hardness of the Ti–Al–Si–N–O coatings exhibited the maximum hardness values of ~43GPa at a Si content of ~5.63 at.% due to the microstructural change to a nanocomposite as well as the solid-solution hardening. Ti–Al–Si–N–O coating with Si content of around 5.63 at.% also showed perfect adhesive strength value of 105.3N. These excellent mechanical properties of Ti–Al–Si–N–O coatings could help to improve the performance of machining tools and cutting tools with application of the coatings. Ti-Al-Si-N-O coatings were applied to insert tools. Their performances were evaluated about cutting-time and cutting-length to Inconel 718 super alloys. Performance of the coated tools were evaluated and compared with different Ti-Al-Si-N-O coatings onto cemented carbide substrates. Especially, the Ti-Al-Si(5.63at%)-N coated tool showed better performance and best tool life in this work.

BP-39 Transparent and Low Resistance Hard Amorphous Carbon Thin Films by HiPIMS for Electronic Applications, ***Kerstin Thorwarth***, *R Ganesan, A Chacko,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland*; M Grein, R Bandorf,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; D McKenzie, M Bilek,* The University of Sydney, Australia*; H Hug,* EMPA - Swiss Federal Laboratories for Materials Science and Technology, Switzerland

High power impulse magnetron sputtering (HiPIMS) was used to deposit optically transparent amorphous carbon thin films with low electrical resistance. The films were deposited on Si substrate. The film of 75 nm thickness exhibit the sheet resistance of 2.5 kW/□ and high visible transmittance of 76 % at 450 nm. The room temperature mobility of the deposited amorphous carbon films lies in the range of 14 - 18 cm2v-1s-1, which is higher than the previously reported values. The X-ray Photoluminescent studies and the optical bandgap by Tauc's method suggest that the bandgap of films lies between 1.75 to 2.35 eV, and depends on the values of negative bias voltage applied to the substrate. The films are totally hydrogen free (H content < 0.7 %) and exhibit densities varied from 2 to 2.6 eV. The measured hardness values are greater than 33 GPa for the films with thickness = 800 ± 40 nm, but deposited at similar deposition conditions. Such properties of the amorphous carbon films have a great potential in the application of transparent conducting electrodes.

BP-40 Reactive Magnetron Sputter Deposition of Bismuth Tungstate Coatings for Water Treatment Applications under Natural Sunlight, *M Ratova,* ***Peter Kelly***, Manchester Metropolitan University, UK*; R Marcelino, C Amorim, P de Souza,* Federal University of Minas Gerais, Brazil

Photocatalysis is a promising method for decontamination of air, water and soil. In particular, photocatalytic purification of wastewater is becoming an increasingly popular process, with the wide range of titanium dioxide-based materials successfully applied as photocatalysts for water treatment application. However, the use of titanium dioxide for efficient water treatment application is restricted with two major limiting factors, namely a relatively high band gap value and low photonic efficiency. The high band gap value results in titania photocatalysts being activated only with ultraviolet (UV) irradiation (<5% of the solar spectrum), therefore, for practical use, additional irradiation sources are required. Consequently, it is rather difficult to achieve high reaction rates, as required when dealing with heavily-polluted industrial wastewater or high throughput systems. As photocatalytic wastewater treatment is aimed at being an economical and practical technique, it is desirable to avoid the extra costs of using artificial light sources in the photocatalytic treatment setup. Use of natural sunlight represents a cheap and sustainable irradiation source, however, as in the case of titania-based photocatalysts, its efficiency can be rather low. Therefore, there is an obvious need for the development of photocatalytic materials based on the use of low band gap semiconductors, combining visible light activity with high photonic efficiency and high surface area.

In the present study narrow band gap semiconductor bismuth tungstate has been deposited onto 2 mm glass beads via reactive magnetron sputtering from a dual source system. The beads were used to increase the surface area, as opposed to flat substrates, and manipulated using an oscillating bowl placed under the magnetrons in order to provide uniform coverage. The atomic ratio of Bi/W was varied through the variation of the power applied to the magnetrons. The deposited coatings were analyzed by SEM, EDX, XRD, XPS and AFM. The photocatalytic properties of the coatings were assessed via their ability to degrade an methylene blue under artificial (fluorescent light) and natural (sunlight) irradiation. The photocatalytic performance of the bismuth tungstate-coated beads was compared to that of titanium dioxide coatings deposited onto identical beads. The results showed that the photocatalytic performance of bismuth tungstate-coated beads was superior to that exhibited by TiO_2-coated beads. Reactive magnetron co-sputtering has been shown to be a promising technique for deposition of narrow band gap bismuth tungstate onto irregularly-shaped substrates for potential use in water treatment applications.

Author Index

Bold page numbers indicate presenter