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

Symposium B Poster Session

BP-8 Large Lattice Strain-caused Change in Nanoscale Plastic Deformation Behavior of Multi-component $(AlCrTaTiZr)N_xC_ySi_z$ Nanocomposite Coatings*, Y Lai, Y Hsiao,* National Tsing Hua University, Taiwan*; **Shao-Yi Lin**,* National Chung Hsing University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

The relationship between the nanostructure and nanoscale deformation behavior of nanocomposite coatings is of importance to their mechanical performance and thus of interest for investigation. In this study, multi-component face-centered cubic (fcc) $(AlCrTaTiZr)N_x$, $(AlCrTaTiZr)NC_y$ and $(AlCrTaTiZr)NSi_z$ coatings were prepared by sputtering, and their nanostructures and nanoscale plastic deformation behavior were characterized using nanoindentation and transmission electron microscopy. The multi-component $(AlCrTaTiZr)N_x$ coating had a simple fcc solid-solution structure and exhibited a typical full dislocation-mediated plastic deformation. With the addition of C or Si (the incorporation of covalent –C or –Si bonds), an fcc nanocomposite structure (with small-angle domain boundaries) formed in the $(AlCrTaTiZr)NC_y$ and $(AlCrTaTiZr)NSi_z$ coatings. Large lattice strains (severe lattice distortions) in the multi-component nanocomposite coatings caused the change of plastic deformation behavior. Under a large indentation stress, low-energy small-angle dislocation structures (with extended partial dislocations or stacking faults) were formed at the small-angle domain boundaries. When the applied stress (the stored high strain energy) was released, many of the stacking faults were removed, and a near-perfect ordered crystal structure was observed. The activities of stacking fault decahedra consisting of highly reversible 1/6 <112> and 1/9 <222> partial dislocations were expected to dominate the plastic deformation and recovery (W_e ~ 76%) of the multi-component $(AlCrTaTiZr)NC_y$ and $(AlCrTaTiZr)NSi_z$ nanocomposite coatings.

BP-9 Advanced Deposition of Hard a-C:Me Coatings by HPPMS using Ne as Process Gas*, K Bobzin, T Brögelmann, N Kruppe, **Martin Engels**,* Surface Engineering Institute - RWTH Aachen University, Germany

Diamond-like carbon (DLC) coatings are used in numerous tribological applications, for example on highly-loaded components of the automotive powertrain. The hardness and roughness of these coatings contribute to the reduction of the component wear. The hardness correlates with the sp^3/sp^2 bond ratio between the carbon atoms, where sp^3 bonds are similar to the diamond structure. The roughness is strongly influenced by the physical vapor deposition (PVD) technology such as the pulsed laser deposition (PLD) or the high power pulsed/impulse magnetron sputtering (HPPMS/HiPIMS). In a previous work it was shown that hard a-C coatings with a low roughness can be deposited by means of HPPMS in a high volume coating unit using Ne as process gas. Furthermore, the doping of hydrogenated a-C:H coatings by means of plasma-assisted chemical vapor deposition (PACVD) with metals is the subject of current research. Significant changes of the coating properties have been found. The formation of nanocomposite a-C:H:Me coatings was reported, which exhibit an increased hardness or reduced plastic deformation, compared to a-C:H coatings. However, a-C:H coatings generally exhibit lower hardness values, compared to a-C coatings. Therefore, the deposition of metal doped a-C:Me coatings by means of HPPMS might contribute to a performance increase in tribological applications. Hence, in the present work a-C:Me coatings were successfully deposited in a high volume coating unit by means of two HPPMS cathodes with Zr and C targets. Furthermore, a correlation with a hybrid process using one direct current magnetron sputtering (dcMS) cathode and one HPPMS cathode was performed. Based on previous works, Ne was used as process gas to increase the ionization in the carbon plasma. Therefore, a high content of sp^3 bonds in the a-C matrix was expected. The average power of the cathode with the Zr target was varied between P = 600 W and P = 1,200 W in order to obtain coatings with different chemical compositions. The resulting coating properties were analyzed by means of nanoindentation, Raman spectroscopy, scanning electron microscopy, X-ray diffractometry and confocal laserscanning microscopy. In summary, the deposition of a-C:Zr coatings by means of HPPMS was successful, since hard coatings with HU > 25 GPa with a low roughness Ra < 0.05 µm are deposited. Finally, the plasma was analyzed by means of energy resolved mass spectroscopy to correlate the coating properties with the composition of the plasma.

BP-10 Plastic Deformation Behavior of Nanostructured CrN/AlN Multilayer Coatings Deposited by Hybrid dcMS/HPPMS*, K Bobzin, T Brögelmann, **NathanChristopher Kruppe**, M Arghavani,* Surface Engineering Institute - RWTH Aachen University, Germany

The physical vapor deposition (PVD) is a commonly applied technology for deposition of hard coating systems such as chromium (Cr)-based nitride coatings on tools and components in tribological applications. In such applications the tools and components are subjected to complex loads, which can lead to elastic-plastic deformation of coating/substrate compounds or crack formation. One approach to increase the life time of compounds under significant loadings is the deposition of nanostructured coatings such as CrN/AlN-nanolaminates with promising hardness and crack resistance. The understanding of the deformation behavior of such multilayers is, however, a key factor for further coating developments. Implementation of nanoscratch analyses in conjunction with high resolution microscopy techniques is an approach to study the tribological behavior of nanostructured coatings and gain information about their plastic deformation under normal and lateral loads. Nanoscratch analyses on the coating system CrN/AlN-nanolaminate deposited on quenched and tempered AISI 420 steel substrate and investigations on the resulted plastic deformation are the subjects of current research. In the present work, a hybrid technology, consisting of direct current and high power pulse magnetron sputtering dcMS/HPPMS, was used for deposition of the coating. The CrN/AlN-nanolaminate was deposited with a bilayer period (thickness CrN + AlN) of Λ = 10 nm. In order to study the plastic deformation of the coating, nanoscratch analyses were performed applying a Berkovich tip. The deformation of coating system under nanoscratch loads was quantitatively analyzed by means of depth profiling using confocal laser scanning microscopy (CLSM). A comprehensive study of the plastic deformation and crack resistance was furthermore performed using scanning electron microscopy (SEM). The SEM analyses were carried out on surface and cross section fractures of the nanoscratch tracks. Scanning transmission electron microscopy (STEM) was applied to explore the micro-scale cracking underneath the nanoscratch tracks. High resolution transmission electron microscopy (HRTEM) was furthermore applied to explore the mechanism of plastic deformation of the investigated coatings. Based on the results, the CrN/AlN-nanolaminate exhibited a significant resistance against plastic deformation and crack formation. Furthermore, the plastic deformation of the investigated coating was explained by reorientation and sliding of grains imbedded in individual layers CrN and AlN.

BP-13 Control and Characterization of Texture in CVD α-Al_2O_3 Coatings*, **Chen Chen**, P Leicht, R Cooper, Z Liu, D Banerjee,* Kennametal Inc., USA

CVD Alumina coating has been one of the most important components of coated cutting tools for many years. Recently, texture control in α-Al_2O_3 has attracted increasing attention due to the possibility to further improve the anisotropic properties such as thermal conductivity and mechanical properties. The influence of process parameters on textures is complex. In this study, we have investigated the influence of nucleation surface condition and catalyst (H_2S) on the texture in CVD α-Al_2O_3 coatings. The α-Al_2O_3 coatings were deposited by CVD in a hot wall vacuum deposition reactor on WC substrates, and were characterized by advanced analytical techniques including SEM, XRD and EBSD. It has been shown that without the addition of catalyst, the crystal orientation in the Al_2O_3 coatings is primarily dominated by the surface condition, while the effect of reactant composition on texture is minimal. On the other hand, in the presence of catalyst during growth, reactant composition also plays an important role in affecting the crystal orientation. This effect is likely due to the strong interaction between the surface the catalyst.

BP-14 New Tools and Models for Industrial Surface and Coating Optimization of Composite Structures*, **Nick Bierwisch**, N Schwarzer,* SIO, Germany

Nowadays the used materials or material combinations in all application fields (e.g. optical, avionic, fun sports or automotive industry) are getting more and more complex. These complex structures are needed in order to increase the performance and lifetime of the components. Such improvements of each part of your complex device, tool or structural element are necessary to reach the performance goals demanded by the desired application. This increased complexity demands extended analyzis and optimization methods. Engineering knowledge and rules of thumb aren't enough anymore.

Proper characterization and optimization of such structures requires invertible mathematical tools of sufficient holistic character. Unfortunately, as such tools are still not available one often finds trial and error or half empirical sensitivity analysis methods in combination with FEM or BEM. Faster tools could help here a lot to save development time and costs [1].

All models (FEM or analytical based) will need exact and generic material parameters for each part of our material system.

A few years ago, SIO developed a model and a dedicated software package called Oliver & Pharr for Coatings (OPfC® [2]) which allows the determination of true generic material parameters (like Young's modulus and Yield strength) for a coating by knowing the parameters of the substrate and all underlying layers.

The software package FilmDoctor® [3] contains analytical models which dramatically speed up the simulation of complex contact situations compared to FEM systems.

The poster will focus on the results of a joint project with Naish international [5] about standup paddling boards and paddles. It will present how the models and software packages are used to improve the performance in critical application conditions dramatically.

References:

[1] N. SCHWARZER, Scale Invariant Mechanical Surface Optimization - Applying Analytical Time Dependent Contact Mechanics for Layered Structures, Proceedings of the 28th International Conference on Surface Modification Technologies, 287-327, SMT 28, June 16th – 18th, 2014, Tampere University of Technology, Tampere, Finland, Publisher: Valardocs, ISBN Number:978-81-926196-1-3

[2] www. [http://siomec.de/OPfC]

[3] www [http://siomec.de/FilmDoctor]

[4] www.naish.com

BP-15 Selection of a Reactive Magnetron Sputtering Method to Produce Films for Biosensors*, Brenda García*, *L Melo-Máximo, O Salas, D Melo-Maximo, A Murillo,* Tecnológico de Monterrey-CEM, Mexico*; J Lin,* Southwest Research Institute, USA*; J Oseguera,* Tecnológico de Monterrey-CEM, Mexico

Three different reactive sputtering methods were evaluated for the production of Al/AlN/Al thin film architectures for biosensing applications. The methods included were direct current, radiofrequency, and modulated pulse power reactive magnetron sputtering. The films were deposited on Si substrates at equivalent power densities and characterized by optical microscopy, glancing angle x-ray diffraction, and scanning electron microscopy + microanalysis. The comparative analysis of the films was based on the most relevant film features for biosensing, namely control of the type of crystalline phases formed, control of preferred orientations, easiness to produce inclined structures, and adhesion to the substrate. Other features such as surface morphology, and density of the films were also considered, as no systematic studies regarding their effect on biosensing have been published.

BP-20 Preparation of Carbon based Multilayered Coatings by means of Pulsed Laser Deposition: Outstanding Mechanical Properties and Enhanced Film Toughness*, René Bertram,* University of Applied Sciences Mittweida, Germany*; M Hess,* Fritz Stepper GmbH & Co.KG, Germany*; H Gruettner, D Haldan, S Weißmantel,* University of Applied Sciences Mittweida, Germany

It will be presented how amorphous carbon coatings can be deposited at low temperatures with mechanical characteristics varying in a wide range depending on deposition parameters and that these properties such as hardness and elasticity can easily be assessed by Raman spectroscopy. For this the indentation hardness and indentation modulus of carbon films deposited at various laser pulse fluences were determined by means of nano indentation and brought into correlation with the peak ratio of the disordered (D-) and graphite (G-) peaks. This offers a fast and simple method to assess H_{IT} and E_{IT} for carbon single layers, for the presented coatings in the range of roughly 20 GPa to 60 GPa and 290 GPa to 620 GPa, respectively.

It will also be shown that the architecture of films designed as multilayered stacks of such different carbon compounds strongly affects the toughness of protective coatings when exposed to high mechanical stresses induced in scratch test or indentation at high loads. Nano indentation measurements showed that this multilayered design does not result in a loss in hardness and elasticity if suitable layer structures are built up. The preliminary computation of stress evolution in the film-substrate system and the actual layer behavior for several layer stack designs will be part of the presentation as well. These coating systems combine a very good adhesion on several metal and hard metal substrates, very high hardness and low abrasive wear, very high elasticity up to 80 % elastic recovery in nano indentation and high crack resistivity in scratch tests and indentation experiments. These superior properties indicate the high potential of laser deposited carbon multilayer as wear protective coatings for cutting tools, bearings and engine components to name but a few.

BP-22 Elastic Constants of Epitaxial Cubic Tantalum Nitride: Thin Film Growth and *ab initio* Calculations*, Gregory Abadias,* Institut P', Université de Poitiers-UPR 3346 CNRS-ENSMA, France*; P Djemia, C Li,* Laboratoire des Sciences des Procédés et des Matériaux (LSPM), France*; Q Hu,* Shenyang National Laboratory for Materials Science, China*; L Belliard,* Université Pierre et Marie Curie-INSP, France*; F Tasnadi,* Linköping University, (IFM), Sweden

Information is still scarce concerning the properties of single-crystal cubic metastable TaN thin films. This work aims at providing some new insights on the elastic and structural properties of TaN epitaxial nitride thin films, especially regarding the influence of defects and nitrogen stoichiometry. 150 nm-thick TaN films were deposited by magnetron sputtering under reactive Ar+N_2 plasma discharges on MgO(001), (110) and (111)- oriented substrates, at a temperature of 650°C. In parallel, *ab initio* calculations were performed in the framework of the density functional theory (DFT) using the VASP software. It has been evaluated how vacancies influence the lattice parameter, the mass density and elastic constants of c-TaN.

The thickness and mass density were determined by x-ray reflectivity measurements, while x-ray diffraction pole figure and reciprocal space maps were employed to study epitaxial orientation and determine the lattice parameters. Elastic constants of thin films can be accurately studied by photoacoustic measurements. The Brillouin light scattering (BLS) technique allows measuring sound velocity of a few kinds of surface acoustic waves (V_{SAW}) in thin films and thus estimating single-crystal elastic constants (ρV^2), in the case of epitaxial films, if the mass density ρ of the film is known. The Rayleigh surface wave is much more dependent on the shear elastic constant C_{44}, thus BLS can provide at least this constant. It is well adapted for thin films and can be conveniently combined with the picosecond ultrasonics technique that measures the sound velocity of longitudinal waves (V_L) that are travelling forth and back within the film along the direction perpendicular to the film plane, i.e. [001], [110] and [111] crystallographic directions.

We used this combination of techniques to measure the elastic constants C_{11}, C_{12} and C_{44} of our epitaxial nitride films. Our results show good agreement between experiments and DFT calculations if defects are taken into account

BP-24 Mechanical and Structural Properties of CrN/AlN Superlattices*, David Holec,* Montanuniversität Leoben, Austria*; M Friak,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic*; Z Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Austria*; M Bartosik, P Mayrhofer,* TU Wien, Austria

Density Functional Theory is a well established tool for predicting structural and mechanical properties of bulk materials. Recent progress facilitated by modern efficient codes and increased computational power has opened doors to studying also extended systems. Examples of such are superlattices, an important design approach of materials with controlled architecture.

In this contribution, we will report on first principles calculations of structural and mechanical properties of CrN/AlN superlattices. The *ab initio* predicted oscillating interplanar distances are corroborated by high-resolution transmission electron microscopy analysis. Further on, we will present fully quantum mechanical calculations of directionally-resolved Young's modulus [1]. We will demonstrate that these yield comparable results with a simple continuum model of Grimsditch and Nizzoli [2]. Also these predictions are in excellent agreement with experimental measurements [1]. Finally, we will discuss the ideal tensile strength of these superlattices.

References:

[1] M. Friak, D. Tytko, D. Holec, P.-P. Choi, P. Eisenlohr, D. Raabe, and J. Neugebauer, New J. Phys. 17, 093004 (2015).

[2] M. Grimsditch and F. Nizzoli, Phys. Rev. B Condens. Matter 33, 5891 (1986).

BP-25 Characterization of the Hard Coating on Gray Cast Iron Under Hydrogen Charging, ***Noe Lopez Perrusquia,*** *M Doñu Ruiz, M Reyes Cortes,* Universidad Politecnica Del Valle De Mexico, Mexico*; C Torres San Miguel,* Instituto Politécnico Nacional - ESIME, Mexico*; V Cortes Suarez,* Universidad Autónoma Metropolitana, Mexico

This work enhance the mechanical properties on pearlitic gray cats iron with hard coating under hydrogen charging. The formation of hard coating was carry out by boron paste dehydrated at temperature of 1173 and 1193 K, with 8 hour exposure time. The characterization of hard coating were using: optical microscopy (OM), X-ray diffraction (XRD), energy dispersive spectrometry (EDS) and the mechanical properties: elastic modulus and hardness were obtained nanoindentation and the adhesion by Rockwell C indentation test. All sample boride were subjected to hydrogen charging and evaluate the behavior of hydrogen on gray cast iron with FeB/Fe_2Bcoating using three point bending results. The mechanical properties enhance the surface on gray cast iron due to hard coatings and increase the bending stress value.

BP-27 Characterization and Growth of B-doped Diamond Grown on HPHT Diamond Substrates using Mode Conversion Type Microwave Plasma CVD, ***Tomoya Sakuma,*** Chiba Institute of Technology, Ogura Jewell Industry Co., Ltd., Japan*; A Suzuki, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω･cm. However, it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} is used as a dopant to synthesize B-doped diamond. Though these dopants are toxic to humans. Trimethyl-borate {$B(OCH_3)_3$} is harmless. Furthermore, accuracy of the machined surface with single crystalline diamond is better than polycrystalline diamond and it is essential for ultra-precision machining and ultra-precision measurement.

In this report, growth and characterization of B-doped diamond on HPHT diamond substrates using mode conversion type microwave plasma CVD were studied.

B-doped diamond was synthesized on single crystalline diamond substrates using mode conversion type microwave plasma CVD apparatus. HPHT diamond substrates were synthesized using high pressure high temperature method and their (1 0 0) facets were crystal orientation. Reaction gases were used CH_4 (15 SCCM) and H_2 (100 SCCM). Trimethyl-borate was used as a boron source. Vapor of trimethyl-borate was carried by H_2 carrier gas into the vacuum chamber with its flow rate of 3 SCCM. Pressure was 20.0 kPa and microwave power was 1.0 kW, respectively. The surface and cross sectional morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy and Laue pattern. Electrical resistivities were measured by the four-point probe method.

In the cross sectional SEM image after laser cutting, epitaxial layer of 0.1 mm thickness was observed.

Raman spectra of B-doped diamond growth layer, the broad peak at around 500, 1230 $cm^{-1}$and the weak peak at 1333 cm^{-1} were observed in each spectra. These peaks were due to high concentration boron inclusions.

As a result of Laue pattern from deposits, clear Laue pattern and weak halo pattern were confirmed.

As a result of the electrical resistivity measurements by the four-point probe method, the minimum electrical resistivitiy was 4.2×10^{-3} Ω･cm.

As a conclusion, single crystalline B-doped diamond was fabricated on HPHT diamond substrate. In the Raman spectra of the film, the peaks caused high boron inclusion were observed.

BP-28 Effects of the Reaction Gas Flow Rates on the Plasma State during Boron-doped Diamond Synthesis, ***Asuka Suzuki,*** *Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity order of 10^{16} Ω･cm. However it was changed to the semiconductor by inclusion of dopants such as boron or phosphorus. However, the liquid B source in the bubbling tank was evaporated at room temperature, it is difficult to control flow rates because it is introduced using H_2 carrier gas, and control range is so narrow. Towards further industrial applications, it is desirable to extend electrical resistivities range by using a relatively less toxic liquid B source. Application to a variety of electronic components to be able to safely control the volume resistivities of the B-doped diamond can be expected to spread.

The investigation was carried on the effects of the reaction gas flow rates on the plasma state during boron-doped diamond synthesis.

Boron-doped diamond films were synthesized using mode-conversion type microwave plasma CVD apparatus. Si substrate was scratched by diamond powder and then cleaned ultrasonically in acetone solution. Reaction gases were used CH_4 and H_2. Vapor of $B(OCH_3)_3$, the boron source, was introduced by H_2 carrier gas into the vacuum chamber. Their flow rate was $H_2/CH_4/H_2$ carrier=100/15/3, 200/30/6, 300/45/9 sccm , respectively pressure was 20.0 kPa and microwave power was 1.0 kW. Reaction time was fixed to 3h. During synthesis, plasma states were estimated using optical emission spectroscopy (OES) . The surface was observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Volume resistivities were measured by the four-point probe method.

As a result of OES, the peaks of B(249nm), BH(433nm), BO(436nm), CH(387nm,431nm), H_α(656nm), H_β(486nm) and C_2(404nm, 406nm, 473nm, 516nm, 563nm, 619nm) were observed for each conditions. In the SEM observation, the grain sizes of deposits were 1 to 3 mm. In the Raman spectra of the deposits, the broad peak at about 500, 1230 cm^{-1} and the weak peak at 1333 cm^{-1} were obtained for each samples . These peaks due to inclusion of high concentration boron in the films. As a result of the electrical resistivity measurements by the four-point probe method, the minimum Volume resistivities of 0.2Ω・cm was obtained. With the reducing of B/Hα, BH/Hα and BO/Hα emission intensity ratio in emission spect ra, volume resistivity is reduced.

As a conclusion, relationship between volume resistivit ies of boron doped diamond and intensity ratio of B-system emissions in OES spectra was suggested.

BP-29 Effects of Pluse Frequency and Duty Cycle on Synthesis of Carbon Nitride using Pluse Microwave Plasma CVD, ***Koudai Yarita,*** Chiba Institute of Technology, Japan*; I Tanaka,* Gifu University, Japan*; Y Sakamoto,* Chiba Institute of Technology, Japan

Carbon nitride has fascinated properties such as high hardness and high current density of field emission. In addition, if a β-C_3N_4 or c-C_3N_4 structure can be synthesized, it is possible to obtain a hardness higher than that of diamond. Our laboratory had investigated to obtain crystalline carbon nitride, and α-C_3N_4 was obtained from a CH_4 – N_2 reaction gas system by microwave plasma CVD. In addition, pulse plasma is possible to control the state of plasma such as electron temperature. Also, pulse microwave CVD is possible to vary particle size and density.

Investigation was carried out on the effects of pulse frequency and duty cycle on synthesis of carbon nitride using pulse microwave plasma CVD。

Carbon nitride was synthesized using an improved microwave plasma CVD apparatus equipped with a water cooled substrate holder and can be selected microwave radiation mode cw or pulse. Si was used as the substrate. A mixture of CH_4 and N_2 was used as a reaction gas system. CH_4 and N_2 flow rates were 2 and 200 SCCM, pressure was 4.0 kPa. The reaction time was 5h. The reaction time was at 5h and the peak microwave power was 1000W. Pulse frequency was varied from 30, 300 and 3000Hz, duty cycle was varied 30, 50 and 70%. The deposits were estimated by Scanning electron microscopy (SEM), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS). The plasma state was estimated by Optical emission spectroscopy (OES).

As a result of SEM observation, crystalline particles were obtained at pulse frequency of 30Hz, duty cycle of 50 and 70%, at frequency of 300 and 3000Hz, duty cycle of 30, 50 and 70%. However, Ball-like particles were obtained at pulse frequency of 30Hz and duty cycle of 30%. Particle densities were from 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle. As a result of Raman spectroscopy, the peak corresponding to Si was observed at pulse frequency of 30 to 3000Hz and duty cycle of 30 to 70%. On the other hand, the peak corresponding to amorphous carbon was observed at pulse frequency of 30Hz and duty cycle of 30%. As a result of XPS, the Si_3N_4 and C-N bond peaks were observed in at all sample. In OES spectra, the peak of CN radical emission was observed for all condition.

Examination result of effect of pulse frequency and duty cycle of microwave plasma on carbon nitride synthesis, crystalline carbon nitride was obtained proper synthesis condition. Also, Particle densities were about 6.2×10^7 to 2.3×10^8 numbers/cm^2. Particle density was lowered with decreasing of duty cycle.

BP-30 Duplex Coating of DLC on High Speed Tool Steel Substrates*, Y Kikuchi,* ***Ryohei Fujita****, Y Sakamoto,* Chiba Institute of Technology, Japan

Diamond-like carbon (DLC) is applied to a wide variety of fields in the industry because of its tribological properties and hardness. However, one of the major issues is the adhesion strength between DLC films and the metal substrate. Many efforts have been made to obtain a higher adhesion strength, such as the formation of an interlayer and the modification of the surface layer. In contrast, radical nitriding is one of the most suitable methods for the pretreatment of duplex coatings, because it possible to increase the surface hardness while maintaining the roughness of the original surface. According to this process, a diffusion layer is formed in the surface region using plasma state control.

High-speed tool steel was used as the substrate. A radical nitridation apparatus was used for the radical nitriding and PNC processes. The conditions for the radical nitriding process were a pressure of 133 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, an external heater temperature of 843 K, and a processing of 60 min. The conditions for the PNC process after radical nitriding were a pressure of 532 Pa, an applied voltage of −380 V, an H_2 flow rate of 50 SCCM, an NH_3 flow rate of 50 SCCM, a CH_4 flow rate of 50 SCCM, an N_2 flow rate of 1 SCCM, an external heater temperature of 843 K, and processing times that were varied from 5 to 10 to 15 min.

After the plasma treatment process, the DLC film was coated onto the substrate using RF magnetron sputtering equipment. The target was graphite, the sputtering gas was Ar, the RF power was 50 W, the pressure was 0.4 Pa, and the processing time was 60 min, respectively. The DLC films were prepared after pre-sputtering under the same conditions for 10 min. The DLC film thickness was 300 nm.

DLC coated on an untreated substrate exhibited extensive delamination and micro-cracks that extended from the vicinity of the crater. High adhesion strength of DLC coatings on high-speed tool steel was accomplished via PNC treatments. In particular, PNC showed the best adhesion strength in this study at 5 min after radical nitriding.

Radical nitriding formed a nitrogen-diffusion layer, followed by the formation of a carbon layer by nitrocarburizing without the formation of a brittle compound layer. It maintained surface roughness compared with the untreated substrate. The resulting DLC films exhibited better adhesion to the treated-steel substrates than to the untreated ones.

BP-33 The Stability of Diamond-Like Coatings under Thermo-Mechanical Conditions*, Q Liu,* ***Xiaoying Li****, H Dong,* The University of Birmingham, UK

Diamond-like carbon (DLC) is an attractive carbon-based coating material for many applications due to their unique combination of low-friction, self-lubrication and high wear resistance in conjunction with good biocompatibility. However, the metastable nature of the amorphous structure restricts the wide application of DLC coatings under harsh conditions. Although there have been many reports on the thermal stability of DLC, limited or no work has been conducted to investigate the stability of DLC coatings under both thermal and pressure conditions.

This work presents a study on the stability of DLC coatings: a-C, a-C:H, a-C:Si and a-C:H:Si thermo-mechanical conditions using a hot isostatic pressure (HIP) furnace to apply both high-temperature and high-pressure. In order to investigate the influence of the applied pressure, thermal stability was also conducted by heating the DLC samples up to 600ºC in air and in argon without pressure. The microstructure of the as-deposited, heat treated and HIPped DLC samples were fully studied using XRD, Raman, FIB/SEM and XTEM; the change of their mechanical and tribological properties were investigated using nano-indentation and tribo-meters.

The experimental results reveal that the high isostatic pressure introduced during HIPping accelerated the graphitization process and hence reduced the stability of these DLC coatings at elevated temperature; the introduced isostatic pressure also reduced the adhesion between the top DLC coatings and the substrates. The mechanisms involved are discussed based on XTEM, XPS and Raman analysis.

BP-38 Growth of DLC Films on the Internal Surface of a Long Metallic Tube Using the PECVD Technique*, E Mitma Pillaca, M Ramirez Ramos, D Lugo González,* ***VladimirJesus Trava-Airoldi****,* National Institute for Spacial Research INPE, Brazil

Plasma Enhanced Chemical Vapor Deposition (PECVD) is a well established method for growing DLC films on substrate with complex shapes, in a fast and efficient way. By this technique, surfaces of mechanical components, for example, are protected from wear and corrosion due to excellent properties that feature this film. However, coating inside tube owns some disadvantages. For example, homogeneous deposition is usually difficult to be achieved in tubes with low aspect ratio. On the other hand, coating in long tubes (some meters) using plasma are not economically feasible due to need for vacuum chambers with greater dimensions than the own tube. In this work, a tube with 0.1 m diameter and 2 m length was prepared to be used as the own vacuum chamber for the growth of DLC film on its internal surface by PECVD technique. Electric tests were performed to study the response of discharge current, as a function of the gas pressure and of the applied voltage in Ar plasma. These results have shown that the plasma inside of the tube is sustained at pressure as low as 5 mTorr and at negative applied voltage as low as -400 V. Different conditions were figuring out for silicon deposition as an interface and also for DLC deposition. Thus, SiH_4 and C_2H_2 has been used as a precursor gas for the silicon and DLC films, respectively. Matching of some parameters in terms of inside pressure, applied bias voltage and gas flow were established in order to get the DLC films with good adhesion, high hardness and good structural quality. A 1500N indentation, nano indentation and Raman spectroscopy analysis has been confirmed the DLC properties deposited on Stainless Steel substrates placed along of the tube. The uniformity along of the tube of DLC films in terms of friction coefficient and growth rate is an important part of this study.

BP-39 Characterization and Tribologic Study in High Vacuum of Hydrogenated DLC Films Deposited using Pulsed DC PECVD System for Space Applications*, D Lugo González,* ***Marco Antonio Ramirez Ramos****, V Trava-Airoldi, P Santana da Silva, E Mitma P., E Corat,* National Institute for Space Research - INPE, Brazil*; C Rodriguez, N Fukumasu,* University of São Paulo, Brazil

DLC is a metastable form of amorphous carbon that has excellent properties such as high hardness, high elastic modulus, chemical inertness, high wear resistance, and low friction coefficient. DLC has been studied as a promising solid lubricant since liquid lubricants are ineffective and undesirable for many space applications. Solid lubricants require performing properly under space environment conditions, such as high vacuum. This paper reports the structure, morphology, adhesion, and high-vacuum tribologcal performance of DLC films with different hydrogen content. The films were deposited by pulsed DC PECVD technique with an additional cathode and using acetylene as a precursor gas. An amorphous silicon interlayer was deposited in order to guarantee the adhesion between coating and substrate. For the films characterization, Raman spectroscopy, Scanning Electron Microscopy (SEM), Rockwell C indentation test, and scratch test were performed. In addition, hydrogen content in the DLC films was determined by Elastic Recoil Detection Analysis (ERDA). Friction coefficient value and wear rate of DLC films in high vacuum conditions were obtained applying loads of 2N and 5N at different sliding speeds. Results showed that DLC films deposited by pulsed DC PECVD can act as a space solid lubricant due to its low friction coefficient value, high adhesion and keeping its structural quality in high vacuum environment.

BP-40 Numerical Analysis on Gas-Pressure and Input-Power Dependence of Substrate-Incident Hydrocarbon Species in Tetramethylsilane Plasmas for Silicon-Containing Diamond-Like Carbon Thin-Films Coatings*,* ***Akinori Oda****, K Ohki,* Chiba Institute of Technology, Japan*; S Kawaguchi, K Satoh,* Muroran Institute of Technology, Japan*; H Kousaka,* Gifu University, Japan*; T Ohta,* Meijo University, Japan

Diamond-like carbon (DLC) films are the hydrogenated amorphous carbon films, which is composed of a mixture of sp^2- and sp^3-bonded carbon. Since this films have excellent material properties in high wear resistance, high hardness, low friction, and chemical stability, the films have been widely used for many technological applications such as automotive, semiconductors, medical devices, and so on. Recently, silicon-containing DLC (Si-DLC) films have been investigated, since the Si-DLC films with lower friction coefficient, compared with conventional DLC films, can be obtained. However, the effect of silicon in Si-DLC films on friction properties has not been clarified. Therefore, the understanding of fundamental properties in tetramethylsilane (TMS, $Si(CH_3)_4$) plasma, which are ion and radical source of Si-DLC films deposition, has been strongly required. Previously, our research group have developed a self-consistent one-dimensional fluid model of capacitively-coupled radio-frequency TMS plasmas, composed of the continuity equations for electron and sixteen TMS-derived ion species, the Poisson equation, and the electron energy balance equation, coupled with the Boltzmann equation solver. And then, the influence of process parameters (e.g. gas pressure, input power) on the plasma properties has been discussed. In this paper, in order to simulate the TMS plasma in realistic geometry (i.e. plasma chamber with realistic size), we developed the axially-symmetric three-dimensional fluid model of TMS plasma, and then examined the process parameter dependence of carbon-containing ion and radical fluxes onto substrate. As a result, it was clarified that three hydrocarbon ion species such as $Si(CH_3)_3^+$, $Si(CH_3)_4^+$ and $HSi(CH_3)_3^+$ are important and dominant ion species with higher density magnitude of 10^9 cm^{-3} in TMS plasma. Other simulation results will be presented in this conference. Acknowledgement: This work was partly supported by KAKENHI (No. 26420247).), and the MEXT-Supported Program for the Strategic Research Foundation at Private Universities 2013-2017 (s131104).

BP-41 The Effect of Substrate Bias on the Structure and Mechanical Properties of the a-C:N Films by a 90°-Bend Filtered Cathodic Arc Plasma (FCAP) System*, **Chih-Chiang Wang,*** National Chung Hsing University, Taiwan*; H Shih,* Chinese Culture University, Taiwan

The carbon-related materials have been attracting lots of attention for decades in flat panel display, optoelectronic devices, etc. due to their unique chemical, electronical, mechanical, and thermal properties. In this study, amorphous nitrogenated carbon (a-C:N) films have been prepared on silicon wafer at 800°C with varying substrate bias upto -650V in a 90°-bend filtered cathodic arc plasma (FCAP) system. The magnetic coil removes neutral carbon atoms and macroparticles from the plasma stream and in this case only the carbon arc discharge is available to form nitrogen ions. XRD showed the peak of (111) plane actually from the nanodiamond nucleated in the a-C:N films and agreed well with the result of HRTEM of d-spacing of 1.76 Å. The hardness of the resulting film was found to be 12.2GPa under an optimal bias of -350V.

The ratio of I_D/I_G of the Raman analysis increased to ~3.5 under the bias of -350V, indicating enriched sp^3-bonded carbon of the graphite domain. The FTIR spectra showed that the higher intensity at $1330cm^{-1}$ of D-band and 709 cm^{-1} of plane bending mode resulting from the graphite-like domains with N ions incorporated; more sp^3 bonds facilitated the completion of the nanodiamond structure. Binding energies of C1s, e.g., 287.6 (sp^3), 285.5 (sp^2), and 284.6 eV (free carbon), and N1s, e.g., 402.0 (N-O), 400.0 (sp^2), and 399.0 (sp^3) eV, have been resolved in the XPS spectra. The ratios of N/C were able to reach as high as 50% at -350V, indicating that higher substrate temperatures together with higher contents of nitrogen promotes the sp^3 clusters in the a-C:N films. These properties and the structure of the a-C:N film are sensitive to the energy of depositing C^+ and strongly dependent on the substrate bias.

BP-42 Stress Optimized Hard Nitride Coatings for High-performance Gear Hobbing*, **Martin Beutner,*** Otto von Guericke University, Germany*; A Lümkemann, M Morstein,* PLATIT AG – Advanced Coating Systems, Switzerland*; B Karpuschewski,* Otto von Guericke University, Germany*; M Jilek, Jr.,* PLATIT AG., Czech Republic*; T Cselle,* PLATIT AG – Advanced Coating Systems, Switzerland

In 2015 the automobile production and therefore also the transmission production exceeds the 90 million. Containing of several gears the manufacturing is of major importance. As the dominating green manufacturing process gear hobbing is applied the most. Here cutting conditions regarding chip thickness and cutting length change continuously within every generating position. Hence, the load at the cutting edge varies critically too and affects abrasive and crater wear on the tool. Nowadays gear hobbing is performed more and more without coolant which intensifies the thermal load and thus the wear phenomena.

To examine the performance of different coatings, cutting trials were carried out using the well-established fly-cutter analogy test. Subsequently the worn out single hob teeth are examined by REM and fringe projection to evaluate the wear phenomena.

To reduce crater wear and to extend the lifetime of gear cutting tools a range of AlCrN-based coatings was deposited in an industrial π411 rotating arc cathodes PVD unit. Significant performance differences between the chemically and structurally modified coatings were found. In this contribution the authors are focusing on the influence of the internal stress of AlCrN-based Hard Nitride Coatings on the wear behavior and tool life for both, high speed steel and solid carbide fly-cutters.

BP-43 Growth of B-Doped Diamond using Hot Filament CVD*, **Mai Imamiya,** Y Sakamoto,* Chiba Institute of Technology, Japan*; Y Takahashi, K Sugiura,* Material Processing Studio Co.,Ltd., Japan

Diamond has excellent physical and chemical properties such as high hardness, high thermal conductivity, optical transmission from UV to IR and chemical inertness. In addition, diamond is well known an electrical insulator with a resistivity of the order of 10^{16} Ω・cm. However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus.

However it was changed to the semiconductor by inclusion of dopant such as boron or phosphorus. Generally, diborane (B_2H_6) or trimethyl-boron {$B(CH_3)_3$} are used as dopant to synthesize boron-doped diamond. In this report, growth of B-doped diamond using Hot Filament CVD.

Hot Filament CVD was used for preparation of diamond. Reaction gases were used CH_4 and H_2. Boron sourse was trimethyl-boron. The synthesis pressure was 4.0 kPa, reaction time was 5 h and distance between the filament and the substrate was kept 8 mm. The surface morphologies of deposits were observed by SEM. Qualities of the deposits were estimated by Raman spectroscopy. Electrical resistivities were measured by the four-point probe method.

As a result of SEM observation, particle was about 1 µm in diameter. Crystal orientation of the deposits was (1 1 1) facet. In Raman spectra, of all the samples, the broad peaks at around $500cm^{-1}$, $1230cm^{-1}$ and the weak peak at 1333 cm^{-1} were observed. These peaks due to the films includes of boron. As a result of the electrical resistivity measurements by the four-point probe method, the lowest electrical resistivitie was 1.6×10^{-4} Ω・cm.

As a result of investigation, boron-doped diamond films were fabricated using Hot Filament CVD and films were orientated to (1 1 1) facets. In the Raman spectra of the films, the peaks caused high boron concentrations were observed.

BP-44 Formation Of Anti-Reflection Double Layers For Si Lens By Atomic Layer Deposition*, **Jaeyeong Heo,** K Kim,* Chonnam National University, Republic of Korea

Increasing demand for mobile services like SNS and movies requires high-speed optical connectivity. In this regard, silicon (Si) photonics takes the center stage in which data is transferred among computer chips by optical rays. Optical transceiver is an integrated circuit that transmits and receives data using optical fiber. For optical transceiver, silicon has recently been highlighted as a material for optical coupling lens due to its low transmission loss and high refractive index. It is expected to increase the coupling efficiency further by fabricating a proper anti-reflection (AR) coating. First, we used Essential Macleod program to simulate the reflectance of single and double-layer anti-reflection coating. Then, we used atomic layer deposition for fabricating anti-reflection coating on Si substrates such as TiO_2 and Al_2O_3. Single layer and double-layer schemes were compared. Detailed structural and optical properties of these AR coatings will be presented.

BP-45 Texture, Mechanical and Electrochemical Properties of Magnetron Sputtered $Cr_{1-x}W_xN/Si_3N_4$ Super Hard Nanocomposite Thin Films for Protective Coatings*, **Ravi Prakash,** D Kaur,* Indian Institute Of Technology Roorkee, India

The effect of tungsten content in $Cr_{1-x}W_xN/Si_3N_4$super hard nanocomposite coatings deposited using reactive DC magnetron sputtering on the silicon substrate (100) has been investigated. The texture, surface morphology, hardness, young modulus and corrosion resistance were studied using X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), atomic force microscopy (AFM), nanoindentation and electrochemical potentiostat respectively. The XRD results show that the $Cr_{1-x}W_xN/Si_3N_4$solid solution formed with preferred orientations of dominant (111) and (200). The crystallite size initially decreased and the increased with the W content. The XRD peaks shifts towards higher angle with the increased as W content increases. Hardness and young modulus of films initially increase and then decrease with increasing tungsten concentration. The maximum values of hardness 42~45 Gpa and young modulus ~500 Gpa were found for tungsten content in the range 4-32 at %. Electrochemical studies of the films indicate that the best corrosion rate (38 nmy) was found at 43% of tungsten content which is excellent compared to other reported value. This study proposed that $Cr_{1-x}W_xN/Si_3N_4$nanocomposite thin films could have future potential as protective coatings.

BP-46 Internal Stress on Adhesion of Hard Coatings Synthesized by Multi-arc Ion Plating*, L Qiu, **Xiaodong Zhu,** K Xu,* Xi'an Jiaotong University, China

Hard coatings have been widely employed in tools, dies and wear-resistant parts. Most commercial coatings are limit in a few microns due to the adhesion problem induced by the stress developed at the film/substrate interface during film deposition and subsequent cooling processes. The residual stress state is considered to be key factor governing the adhesion of thick hard coatings. It is significant to understand the relationship between the residual stress and the bonding strength of hard coatings.

In this work, one group of TiN coatings was prepared by multi-arc ion plating (MAIP). In order to investigate the influence of the residual stress on coating's adhesion, all coatings were synthesized with the same pretreatment and interlayer to obtain an identical interfacial state. During the coating deposition, the working pressure and bias voltage were varied respectively to obtain different residual stress. The average residual stress of the coatings was calculated from the bending deformation of the sliced steel substrate. The bias voltage is shown to have a strong impact on the residual stress of coatings. As the bias voltage increases from -10 V to -200 V, the residual stress increases from -1.8GPa to -3.2 GPa for the coatings with thickness of 10 µm, and the corresponding critical load by scratch test decreases from 60N to 40N. The working pressure is another important parameter that affects the residual stress. The stress level of the coating deposited under 6 Pa is -1.8 GPa in comparison to -2.2 GPa which deposited under 1 Pa, and the critical load by scratch is higher. Higher bias or lower working pressure may cause higher ion energy transferred to deposition ions, and produce fine grain structure.

Another group of TiN coatings with five thicknesses (3.7µm, 5.8µm, 9.7µm, 15.5µm and 25µm) was coated under same parameters and different deposition time. Low critical loads by scratch and indentation tests are obtained for the thick coating indicating the high interfacial stress, yet its average residual stress is lower. Finite element analysis was employed to reveal the stress at the interface. It is found that high residual stress results in a lager shear stress at the interface. This implies that the accumulated residual stress is more appropriate than the average one in characterizing the residual stress effect on coating adhesion for those with different thicknesses.

BP-47 Diamond-like Coatings using High Power Impulse Magnetron Sputtering, ***Tomas Kubart***, *A Aijaz,* Uppsala University, Sweden

Diamond-like carbon (DLC) coatings exhibit excellent mechanical, electrical and optical properties such as high hardness, low friction coefficient, high refractive index which make them attractive for a wide range of applications from cutting tools to engine components. The main limitations of existing DLC solutions stem from its high internal stresses and limited thermal stability. High internal stresses in excess of ~10 GPa limit the maximum achievable thickness due to poor adhesion and limited thermal stability makes DLCs unsuitable for high temperature applications. In order to address these issues, strategies for developing a new generation of DLC coatings exhibiting low-stresses, high hardness, good adhesion and good thermal stability are desired.

This work deals with the development of a deposition process for DLC coatings based on High Power Impulse Magnetron Sputtering (HiPIMS). We synthesize DLC coatings using Ne-based HiPIMS process to enhance the ionization of C. For comparison, plasma and film properties using standard Ar-HiPIMS process are also studied.

The plasma properties investigated by time-resolved Langmuir probe measurement reveal that Ne-based HiPIMS discharge provides high density plasma with higher electron temperature that entails a higher C^+ ion fraction as compared to Ar-HiPIMS discharge. A direct consequence of higher C^+ ion fraction is the higher mass densities (up to 2.7 g/cm^3) obtained using Ne-HiPIMS process. Surprisingly, even the Ar-HiPIMS process led to a pronounced increase in the density (2.5 g/cm^3) albeit lower than in in Ne-HiPIMS. Results from time-resolved behavior of electron temperature and plasma density are discussed with respect to the properties or resulting films for both process gases.

Acknowledgement: The work has been carried out in frame of M-Era.Net project TANDEM supported by VINNOVA.

BP-48 Synergistic Effect of Cu/Cr Co-doping on the Wettability and Mechanical Properties of Diamond-like Carbon Films, ***Lili Sun***, *P Guo, X Li, A Wang,* Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, China

By choosing carbide-forming element Cr and non-carbide-forming element Cu as co-doped metal elements, we firstly fabricated Cu and Cr co-doped diamond-like carbon (Cu/Cr-DLC) films using a facile hybrid ion beam deposition system. The effect of Cu/Cr co-doping on wettability and mechanical properties of DLC films were focused. The resultant Cu/Cr-DLC films were shown to afford good hydrophobicity and superior mechanical performance. In particular, the film with Cu11.88%Cr6.57% (at.%) exhibited a relatively high water contact angle of 103.6°, lower residual stress of 0.89 GPa and high hardness of 13.44 GPa. The combined structural analysis demonstrated that the synergistic Cu/Cr co-doping resulted in the critical and significant relaxation of distorted C-C bond length, which ultimately caused the reduction in residual stress. Due to the formation of hard Cr carbide nano-particles in amorphous carbon matrix, the films maintained the high value of hardness. Noted that the interesting wetting variety from hydrophilic to hydrophobic state was attributed to the enhanced surface graphitization and emergence of copper oxidation phases. The film topographical structure could also promote the hydrophobicity when the maximum height of roughness was in a certain range. These results provide an expected robust method to make DLC film a promising protective coating for long lasting hydrophobic application and related harsh fields.

BP-49 Novel Technology for ta-C Coatings Deposition, ***Jan Kluson***, *M Jilek, Jr.,* PLATIT a.s., Czech Republic

Platit presents a novel patented technology enabling to prepare ta-C coatings with their unique properties in industrial scale. The technology is based on the cathodic vacuum arc burning on the cylindrical rotary cathode. The achieved coatings are designated as DLC^3 and represent the 3rd generation in the Platit DLC family. These coatings are characterized by very high mechanical hardness around 80GPa. Measurements of microhardness were complemented with Raman spectrometry which revealed sp^3 to sp^2 ratio up to 85%. DLC^3 coatings are further characterized by very low friction coefficient and low roughness. The given parameters can be achieved with a new focusing magnetic field source PisCoat (Pi smooth Coating) for particle filtering. Various applications of the technology will be shown.

BP-53 Evaluation of Plant-Extract-Based Metallic Nanoparticles for Corrosion Inhibition of Metallic Component, ***Omotayo Sanni***, *A Popoola, O Fatoba,* Tshwane University of Technology, South Africa

Corrosion of metal is costly material science problems which originate from the day of metal discovery. Corrosion inhibitor usage is an effective way of addressing metallic corrosion in aggressive environments but continued usage of synthetic chemicals for inhibiting corrosion is indefensible as a result of toxicity of the chemicals to the environmental ecosystem. Eco-friendly corrosion inhibiting alternatives, including plant-extract usage, are therefore needed. Characterization of this nanoparticles material will be studied using. Ultra violet analysis, morphology by SEM-EDS and TEM analyses, phase composition by XRD analyses, inorganic element constitute analyses by RAMAN spectroscopy and organic element constituents' analyses by FTIR spectroscopy. Effect of the nanoparticles on metallic samples in different aggressive environment will be studied in the laboratory using weight loss method. The samples exposed to the inhibitors showed a lower corrosion rate values and excellent polarization resistance as compared with the corrosion rate samples without inhibitor. Grey relational used in this research correspond with the experimental results.

BP-55 Deposition of Crystalline Cr_2O_3 Coatings by Reactive Radio-frequency Magnetron Sputtering, *M Mohammad Taheri, Q Yang,* ***Jesus Corona Gomez***, University of Saskatchewan, Canada

Reactive radio-frequency magnetron sputtering technique was employed to study the deposition conditions for crystalline chromium oxide films with Cr_2O_3 stoichiometry. Chromium oxide coatings with a thickness of 1-2 micrometers were deposited on Silicon wafers under various oxygen partial pressures and substrate temperatures. The effect of deposition parameters on the chemical composition, crystal structure, microstructure, phase composition, and hardness of coatings were investigated by electron dispersive spectroscopy, X-ray diffraction (XRD), scanning electron microscope, Raman spectroscopy, and nanoindentation, respectively. Crystalline coatings obtained by increasing the oxygen flow rate or the substrate temperature, however vitrification of coatings was triggered again by flowing more oxygen. No coatings could be deposited at temperatures higher than 300 ° C due to volatilization behavior of chromium oxides at high temperatures. The results illustrated that pure crystalline Cr_2O_3 coatings with highest hardness could be obtained at a substrate temperature of 300 °C and an oxygen content of 6 vol. %.

BP-56 Cerium Doping of Ti-Al-N Coatings for Excellent Thermal Stability and Oxidation Resistance, *H Asanuma,* Mitsubishi Materials Corporation, Japan; *P Polcik, S Kolozsvári,* Plansee Composite Materials GmbH, Germany; *F Klimashin, H Riedl,* ***Paul H. Mayrhofer***, Institute of Materials Science and Technology, TU Wien, Austria

Ti–Al–N thin films are well established due to their outstanding thermo-mechanical properties. Nevertheless, this system is still a subject of many research activities to further enhance their oxidation resistance and thermal stability. The addition of reactive elements, such as Cerium, can significantly improve especially the oxidation resistance of various materials. Therefore, we study in detail the impact of Ce (2 at% alloyed to powder metallurgically prepared $Ti_{0.50}Al_{0.50}$ targets) on growth processes, structure, mechanical properties, thermal stability, and oxidation resistance of magnetron sputtered $Ti_{1-x-y}Al_xCe_yN$ coatings prepared with DC bias potentials of U_{bias} = -25, -50, -75, and -100 V. The deposition rate is significantly increased by a factor of ~1.75 (U_{bias} = -25 V) to 1.45 (U_{bias} = -100 V) when using $Ti_{0.49}Al_{0.49}Ce_{0.02}$ instead of $Ti_{0.50}Al_{0.50}$ targets. Furthermore, also the hardness of the resulting single phase face centered cubic $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ is with ~35.2 GPa above that of $Ti_{0.42}Al_{0.58}N$ with ~33.7 GPa, for coatings on polycrystalline Al_2O_3 and U_{bias} = -50 V. Coatings on steel substrates typically show ~5 GPa higher values.

All temperature dependent characteristics of $Ti_{0.42}Al_{0.58}N$ are improved significantly by the addition of Cerium. Wurtzite-structured AlN formation within $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ can only be detected at T_a = 1100 °C, about 200 °C higher as for $Ti_{0.42}Al_{0.58}N$. Their peak-hardness, due to spinodal decomposition of the supersaturated cubic phase is ~37.0 GPa with T_a = 900 °C, as compared to 34.6 GPa with T_a =800 °C for $Ti_{0.42}Al_{0.58}N$. Additionally, even after exposure to ambient air at 950 °C for 3 h, still > 50 % of the $Ti_{0.43}Al_{0.55}Ce_{0.02}N$ coating is intact (below the ~1.2 µm thin oxide scale), whereas $Ti_{0.42}Al_{0.58}N$ is already fully oxidized.

Based on our results we can conclude, that Ce-doping improves the deposition characteristics and mechanical properties as well as thermal stabilities (incl. oxidation resistance) of Ti–Al–N, to be used as protective coatings for a wide range of high-demanding applications.

BP-57 Arc Evaporated W-alloyed Ti-Al-N Coatings for Improved Thermal Stability, Mechanical, and Tribological Properties*, S Glatz,* Institute of Materials Science and Technology, TU Wien, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Kolozsvári,* Plansee Composite Materials GmbH, Germany*; C Koller,* ***Helmut Riedl,*** Institute of Materials Science and Technology, TU Wien, Austria*; P Mayrhofer,* Christian Doppler Laboratory for Application Oriented Coating Development at the Institute of Materials Science and Technology, TU Wien, Austria

The protection of various tools and components through wear resistant coatings is imperative in highly efficient and precise industrial manufacturing processes. Especially, physical vapour deposited $Ti_{1-x}Al_xN$ and $Cr_{1-x}Al_xN$ coatings have been commonly used as hard protective coatings due to their outstanding thermal stability and mechanical strength. However, to increase the applicable working temperatures by simultaneously enhancing the wear performance (e.g., to allow for higher cutting speeds) further improvements are required.

Therefore, we studied in detail the impact of tungsten (W)—in combination with the substrate bias potential (U_{bias})—on the thermo-mechanical properties and wear performance of arc evaporated

$Ti_{1-x-y}Al_xW_yN$ thin films. With increasing W content the quality of our coatings significantly increases due to pronounced reduction of growth defects (quantity of macro particles). All coatings studied crystallise in a supersaturated, single-phased face-centred cubic $Ti_{1-x-y}Al_xW_yN$ structure and their hardness (H) increases whereas the indentation modulus (E) decreases with increasing W content. This results in increased H^3/E^2 values, with a maximum of 0.19 GPa for $Ti_{0.50}Al_{0.41}W_{0.09}N$ prepared with U_{bias} = -120 V (H ≈ 35 GPa, E ≈ 483 GPa). All W-alloyed coatings exhibit wear rates below $2 \cdot 10^{-5}$ mm³/Nm during our dry sliding pin-on-disk tests against alumina balls at room temperature, with a tendency for reduced values if more droplets are present. The highest thermal stability, with respect to the decomposition of the supersaturated $Ti_{1-x-y}Al_xW_yN$ phase towards the stable constituents (at high temperature) TiN, AlN, and W, is obtained for $Ti_{0.53}Al_{0.42}W_{0.05}N$ prepared with U_{bias} = -80 V. Here, the formation of the wurtzite-structured AlN can be delayed to 1000 °C after 60 min lasting isothermal annealings in vacuum.

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