Monday Morning, May 20, 2019

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-1-MoM

PVD Coatings and Technologies I

Moderators: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), **Jyh-Ming Ting**, National Cheng Kung University, **Qi Yang**, National Research Council of Canada

10:40am **B1-1-MoM-3 Structural, Optical and Wettability Properties of Thermally Evaporated CaF_2, MgF_2 and CaF_2/MgF_2 Films***, **Ravish Kumar Jain**, J Kaur, A Khanna,* Guru Nanak Dev University Amritsar India, India

In this work, thin films of CaF_2, MgF_2 and their multilayered stacks have been deposited on microscopy glass substrates by thermal evaporation and their structural, optical and wettability properties have been studied. Four different sets of samples i.e. glass/CaF_2, glass/MgF_2, glass/CaF_2/MgF_2 and glass/CaF_2/MgF_2/CaF_2/MgF_2 were prepared. X-ray diffraction studies revealed that crystalline CaF_2 film grows in glass/CaF_2 and in the 2-layer stacked glass/CaF_2/MgF_2 samples whereas, it grows in the amorphous phase in 4-layered stacked glass/CaF_2/MgF_2/CaF_2/MgF_2 sample. On the other hand, MgF_2 layer in all the samples grows in the amorphous phase. Field emission scanning electron microscopy (FESEM) was used to study the surface morphology and thicknesses of the samples. The surface FESEM image of CaF_2 film shows very small flake-like morphology whereas the MgF_2 film has a smooth morphology due to its amorphous nature. The cross-sectional FESEM images found that the thickness of the pure CaF_2 film (102 nm) is lesser than that of pure MgF_2 film (127 nm). The optical transmittance and reflectance properties were studied by UV-Vis spectroscopy which confirmed that all the films possess good anti-reflecting properties. The average specular reflectance values in the wavelength range: 350-1100 nm are 10.8%, 7.9%, 8.6%, 6.4% and 8.4% for bare glass slide, MgF_2, CaF_2, 2-layer and 4-layer stacked films respectively which confirms that the reflectance decreases with the top coating of the fluoride films. The water contact angle studies were carried out to study the wettability properties of the samples and it is found that the pure $CaF_2$and MgF_2 films are hydrophobic with an average water contact angle 131±1° and 98±1°, respectively. The wettability properties of the 2-layer and 4-layer stacked structures were found to be completely different compared to single layer thin films and showed hydrophilic nature with water contact angles of 20±1° and 47±1° respectively with reflectance values that were comparable to those of MgF_2 and CaF_2 films. It is concluded that CaF_2 films have a very good potential to be used as hydrophobic anti-reflecting coatings and stacking with other well known optical material such as MgF_2, can tailor its wettability and anti-reflecting properties.

11:00am **B1-1-MoM-4 Metal / ScAlN / Interdigital Transducer (IDT)/ $LiNbO_3$ Multilayer Structure for High K^2 Surface Acoustic Wave Device***, **Yu Hsuan Huang**,* National Cheng Kung University, Taiwan*; S Wu,* Tung-Fang Design University, Taiwan*; J Huang,* National Cheng Kung University, Taiwan

We reported a high electromechanical coupling coefficient (K^2) Surface acoustic wave (SAW) devices on metal / ScAlN/interdigital transducer (IDT)/ $LiNbO_3$ structure and we used Al/ Ti / Mo as metal layer. The $Sc_{0.31}Al_{0.69}N$ films in different thickness (0.5, 1, 1.5, 2 μm) were deposited on Y-128˚ lithium niobate ($LiNbO_3$) substrate which possesses high K^2 by reactive magnetron co-sputtering using Sc and Al as targets. In the previous research, the replacement of Al by Sc increases piezoelectricity because of the phase transition. The $Sc_xAl_{1-x}N$ films 2D-XRD result showed that high c-axis (002) orientation and 2D-XRD χ angle showed that there is a critical thickness. The (002) plane tilting from a normal direction of $LiNbO_3$ substrate before 1μm and it growth normal direction after critical thickness. The SEM cross-section result showed that ScAlN films have tilting form substrate and have columnar structures. The SEM top view indicated that spindle-like morphology and grain cover the whole surface when thickness over 1μm. The piezoelectric coefficient (d_{33}) measured the highest value 42.8 pm/V of $Sc_{0.31}Al_{0.69}N$ film. The K^2 values are increasing with the metal layer deposited on. The highest K^2 value is three time larger than IDT/ $LiNbO_3$ (4.9%) structure. The metal / ScAlN/ IDT/ $LiNbO_3$ structure have a great potential in high frequency and high K^2 SAW devices.

11:20am **B1-1-MoM-5 Sputter Deposited W-HfO_2 for Solar Absorbers***, **Lih-Yang Chiu**, J Ting,* National Cheng Kung University, Taiwan

Tungsten-doped Hafnium oxide W-HfO_2) coatings were deposited using RF and DC reactive magnetron sputtering techniques. Stainless steel (.5 x .5 cm) was used as substrates for solar absorberW-HfO_2 coatings. In this works, various deposition parameters including sputtering power, O_2 flow rate, and deposited time were investigated. The resulting coatings therefore exhibit various compositions, crystal structures, grain sizes, and thicknesses. The obtained coatings were examined using field emission scanning electron microscopes, X-Ray diffraction, X-Ray photoelectron spectroscopy, Colorimeter technique (CIELab 1976 color space), UV/vis/NIR spectrometer, and Fourier-transform infrared spectroscopy. Effects of the material characteristics on the coating performance is discussed.

Keywords: W-HfO_2, reactive magnetron sputter, solar selective coatings.

11:40am **B1-1-MoM-6 High Power Impulse Magnetron Sputtering using Deep Oscillatory Micro Pulses for Surface Engineering***, **Jianliang Lin**,* Southwest Research Institute, USA **INVITED**

As one version of high power impulse magnetron sputtering (HiPIMS) technique, deep oscillation magnetron sputtering (DOMS) is developed from the early modulated pulsed power magnetron sputtering (MPPMS) technique. In DOMS, large oscillatory high power micro-pulses (e.g. tens of μs) are generated within long modulation pulses (up to 3~5 ms). The magnitude of the peak power can be adjusted by controlling the on and off times of the oscillatory micro-pulses. By using optimal combinations of on and off times of these oscillatory micro-pulses, virtually arc free reactive HiPIMS process can be achieved for many insulating coating materials (e.g. Al_2O_3, AlN, SiO_2, etc.). The paper presents an introduction of the DOMS technique with key processing features and parameters. The observation and mechanisms of generating arc-free discharge for reactive sputtering insulating coatings using deep oscillatory micro-pulses will be discussed . Recent technological development in DOMS for surface engineering will be presented. Specific examples will be focused on high rate deposition of transparent metal oxide coatings for optical and wear resistant applications, super hard hydrogen free diamond like carbon (DLC) coatings for low friction and wear applications, strongly (0002) textured AlN films for piezoelectric applications, and thick superlattice nitride coatings for solid particle erosion and high temperature wear protection. It is shown that the enhanced target ionization in combination with excellent process stability in DOMS enables the deposition of a variety of high quality coating materials with improved properties.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B3-1-MoM

Deposition Technologies and Applications for Diamond-like Coatings I

Moderator: Klaus Böbel, Bosch GmbH

10:20am **B3-1-MoM-2 On the Deposition and Properties of Carbon-based Multilayer Systems Prepared by PLD***, **Steffen Weißmantel**,* University of Applied Sciences Mittweida, Germany*; M Hess,* Fritz Stepper GmbH & Co. KG, Deutschland, Germany*; R Bertram, D Haldan, T Warnk, J Maus, S Rupp,* University of Applied Sciences Mittweida, Germany

The layer deposition technique Pulsed Laser Deposition (PLD) provides a feasible way to produce pure carbon films in a wide range of mechanical properties. These properties cover, depending on the deposition parameters, indentation hardness H_{IT} from 20 GPa up to 70 GPa and indentation modulus E_{IT} from 300 GPa up to 700 GPa. As we are going to show, the variation of these mechanical properties over wide ranges can be correlated with the Raman spectra of the films. In particular, the intensity ratio of the disordered and graphitic peak provides an efficient way to determine the mechanical properties of the hydrogen free amorphous carbon films.

Based on the fact that the variation of hardness can be done simply by varying the laser fluence, layered structures consisting of sublayers of alternating or continuously changing sp^3 content and hardness were deposited. The periodicity of the bilayer stacks were varied from 500 nm down to 2.5 nm resulting in an immense increase of interfaces up to 800 since the total film thickness was kept constant at 2 micron. Keeping the ta-C film component constant at some 65 GPa , the hardness of the soft a-C layer component has been changed in the range of 20 up to 50 GPa. The toughness and resistivity against wear and cracking of these multilayered films were evaluated and compared to super-hard single ta-C films. We could show that properly designed multilayered structures have in this respect much improved properties compared to the single layer. In scratch tests, these multilayers show besides an excellent adhesion to various substrate materials a significantly improved, very high cohesive breaking strength. In addition, by testing the abrasive wear of such coating systems against polycrystalline diamond suspension using calotte grinding and against various ceramics and metals using a pin-on-disk tribotester, superior durability was identified, surpassing conventional wear protection layers by up to 3 orders of magnitude.

A computational analysis of the stress distribution in the film substrate systems was used to get an idea of the positions and values of stress under different load scenarios. Based on that film architectures were designed and deposited that show optimized stress distributions to relieve the strain at the substrate layer-system interface. It will be shown that a proper film design enables the deposition and application of extremely hard, durable and yet tough diamond like carbon coating systems. These outstanding layer properties such as high hardness, elasticity, toughness and wear resistance show the great potential of such carbon-based films, i.e. for application as wear protection coatings.

10:40am **B3-1-MoM-3 Improved Adhesion of a-C and a-C:H Films with a CrC Interlayer on 16MnCr5 by HiPIMS-Pretreatment***, W Tillmann,* ***Nelson Filipe Lopes Dias****, D Stangier,* TU Dortmund University, Germany*; W Maus-Friedrichs, R Gustus,* Technical University Clausthal, Germany

A high adhesion of amorphous carbon films to steel substrates remains a challenging task, sustaining continuous research efforts to improve the adhesion strength. Besides the interlayer system and the substrate material, surface pretreatments have a crucial role on the adhesion behavior. Within this context, the influence of the High Power Impulse Magnetron Sputtering (HiPIMS) pretreatment on the adhesion of hydrogenfree (a-C) and hydrogenated (a-C:H) amorphous carbon films with a chromium carbide (CrC) interlayer on 16MnCr5 steel is investigated. The plasma treatment consisted of 30 min Ar ion etching as well as a sequential 5 min of HiPIMS-pretreatment with a Cr cathode, subsequently comparing this procedure to a procedure without the HiPIMS technique. The impact of the HiPIMS-pretreatment on the structure of the film was systematically analyzed by taking the CrC interlayer as well as the entire film structure into consideration.

The adhesion strength of the a-C and a-C:H films is significantly improved by HiPIMS-pretreating the 16MnCr5 steel. In scratch tests, the critical load L_{c3} for a total film delamination increases from 43 ± 4 to 59 ± 3 N and from 48 ± 2 to 64 ± 3 N for the a–C and a–C:H film. The improved adhesion behavior of the carbon films is ascribed to the increased adhesion of the CrC interlayer, which did not delaminate when scratched with a load up to 159 ± 18 N . Complementary Rockwell indentation tests reveal that the HiPIMS-pretreatment improves the adhesion class from HF6 to HF4 and from HF5 to HF3 for a–C and a–C:H. The enhanced adhesion is essential to exploit the properties of a–C and a–C:H films in applications with high loads. In conclusion, the HiPIMS-pretreatment has proven to be a promising technique to increase the adhesion strength of carbon films.

11:00am **B3-1-MoM-4 Properties Of Diamond-Like Carbon Films With Incorporated CVD-Diamond Nanoparticles***,* ***Rebeca Falcão,*** Institute of Science and Technology, Federal University of São Paulo (UNIFESP), Brasil*; C Wachesk,* Federal University of São Paulo, Brazil, Brasil*; T Taiariol,* National Institute for Space Research, Brazil*; G Vasconcelos,* Instituto de Estudos Avançados, Brazil*; E Corat, V Trava-Airoldi,* National Institute for Space Research, Brazil

Diamond-like carbon (DLC) films have been extensively applied as a surface coating due their attractive mechanical, chemical and tribological properties. The properties of the a-C:H films can be significantly enhanced by the presence of diamond nanoparticles in their structure with some apparent advantages by combining hardness, low roughness, coefficient of friction, biocompatibility, etc., of both materials. However, functionalization of diamond nanoparticles and their severe big clusters formations represent some challenges to be overcome. Therefore, the innovative aspect of this work is the growth of DLC films with incorporated CVD nanodiamonds (NDs), obtained by high energy ball milling technique with controlled sizes and functionalization avoiding a lot of clusters formation. In this work, CVD NDs, obtained at the first time, were chemically processed due to the high levels of contamination by using fluoric and nitric acid chemical attack. The DLC films were deposited on a metallic substrate by using a modified Pulsed DC Plasma-Enhanced Chemical Vapor Deposition (PECVD) technique, and the incorporation of the NDs into the DLC films structure was carried using a colloidal solution of NDs and DLC films precursor. The influence of the CVD NDs size on physical and chemical properties of the hybrid film, such as hardness, coefficient of friction, morphology, and chemical inertia were investigated. Nanoparticles size and the level of purity was analyzed by dynamic light scattering and X-Ray diffractometry (XRD) technique, respectively. The hybrid DLC films were characterized by scanning electronic microscopy-field emission gun, XRD and Raman scattering spectroscopy. Also, the qualitative adhesion of the film was analyzed by RHC 1500 N indentations in accordance with the VDI3198 standard. An apparent application with preliminary results is also a part of this work.

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11:20am **B3-1-MoM-5 Influence of the Argon as an Ignitor and an Agent on DLC Properties Growth at Pressure as Low as 3 x 10^{-4} mbar by Modified Pulsed-DC PECVD Method***,* ***Vladimir Jesus Trava-Airoldi,*** *K Nass, E Corat,* National Institute for Space Research, Brazil*; N Fukumasu,* Sao Paulo University, Brazil*; M Ramirez,* University of Vale do Paraiba, Brazil*; G Capote,* National University of Bogota, Colombia

As reported for many years, hydrogenated DLC films (a-C:H) have been a choice of a protective coatings for many applications due to their set of superior mechanical, chemical, tribological and biological properties such as: high hardness, high wear resistance, low coefficient of friction, high chemical inertness, good biocompatibility, bactericide, etc.. However, in order to improve the adhesion between the DLC and the different metals substrates a huge modification of a Pulsed DC PECVD technique has been obtained introducing an additional cathode working as electron and ion confinement. With these modifications pressure as low as 10^{-3} mbar allow operating in collisionless regime improving not only the adhesion but also a set of DLC proprieties cited above. So, in this work we present studies concerning more improvement properties of the DLC films as a function of confinement of electrons and ions parameters in a plasma discharge by using argon as an ignitor gas for the interlayer precursor and keeping it during all the process of DLC deposition. In this case the best conditions of collisonless operation was reached at pressure as low as 3.10^{-4} mbar. Basically, due to the condition of operating in very low pressure, this technique allows to grow the DLC film with very good uniformity and higher hardness, higher adhesion, lower coefficient of friction, less porosity and, also, provide to be able to get a DLC deposition in the form of multilayer, like thicker films, promoting less residual stress. So, studies at the first time, of DLC with superior properties has been carried out from PECVD technique. More specifically, studies of the DLC film properties as a function of the argon buffer gas density and as a function of bias voltage has been done. Raman scattering spectroscopy, Rockwell indentation, nano indentation, FEG, and trybological analyses are discussed. Also, the operating parameters of this modified PECVD system are well controlled, so that a scaling up studies will also be presented as an important part of this work.

Keywords: DLC films; DC pulsed PECVD; additional cathode; argon ignitor, mechanical and trybological properties.

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B1-2-MoA

PVD Coatings and Technologies II

Moderators: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), **Jyh-Ming Ting**, National Cheng Kung University, **Qi Yang**, National Research Council of Canada

1:40pm **B1-2-MoA-1 Harlan™: High Rate-High Density Pulsed Magnetron Sputtering Source for Depositing Metal & Ceramic Coatings for Industrial Applications.**, *B Abraham, **Roman Chistyakov**,* Ionex Corp, USA

A patented & proprietary high density/high rate magnetron deposition source developed in-house from the ground up. The development includes a newly designed high-density plasma generator and an improved magnetron deposition source far more superior to any conventional magnetron technology in the market today. The data presented will include deposition rates and X-SEM images of different thin films such as DLC , High Rate Metal Nitrides (MeN) and High Rate Metal Oxide (MeO), Highly Ionized Metal (Me).

2:00pm **B1-2-MoA-2 Arc Sources for Low Defect Coatings and High Target Utilization**, ***Victor Bellido-Gonzalez**, D Monaghan, B Daniel, R Brown, J Price, A Azzopardi,* Gencoa Ltd, UK

Cathodic arc deposition, also known as arc ion plating or arc evaporation, is a PVD technique utilizing arc sources to deposit non-reactive and reactive coatings, such as carbide, nitride, carbonitrides, diamond like carbon, etc. Compared to traditional magnetron sputtering, denser coatings can be obtained by arc sources due to a higher degree of ionization and thus higher potential energy of the vapour flux towards the substrate. Also the ability of generating metal ions enables adhesion enhancement in some particular processes, like hard coating on cutting tools. Usually, target evaporation by arcs rather than momentum transfer in sputtering leads to a higher deposition rate in arc deposition, and provides a higher degree of heat on the substrate, which is beneficial for some processes. Unlike in Reactive Magnetron Sputtering, reactive arc has a very wide window of process conditions for a successful reactive process. However the deposition conditions all affect the arc parameters and the levels of macroparticle defect on the coating. Different solutions for filtering of the macroparticles have been devised, such as venetian blinds and Magnetic Guidance Filters. It is desired however that the basic level of macroparticles is reduced at its origin.

This work aims to obtain low defect coatings without using macroparticle filters and to obtain high target utilization by controlling the arc travelling. A 125mm circular arc source with optimized design will be employed for nitride deposition. Reliable arc triggering has been realized without mechanical trigger. The arc source will be powered by an arc generator with the capability to vary the arc current during deposition. A small but effective and easily adjustable controller will be used for varying the magnetic field. The effects of varying the arc current and the magnetic field on the defect generation and the target erosion will be investigated. SEM/EDX will be used to characterize the coating defects.

2:20pm **B1-2-MoA-3 Cutting Tools in the Era of Industrial Internet of Things and Additive Manufacturing**, ***Aharon Inspektor**, A Rollett, P Salvador,* Carnegie Mellon University, USA

The Industrial Internet of Things (IIoT), which involves multi-level internet-connectivity of machines and systems, and additive manufacturing (AM) of complex 3D printed items hold great promise to revolutionize the manufacturing industry. In this paper we will discuss the impact of IIOT and AM on the machining sector and anticipated challenges and opportunities for cutting tools and hard coatings. We will examine how sensors that provide real-time internet-connected feedback on the conditions of the cutting edge will allow confident increase in cutting speeds and other machining parameters. This will lead to expansion of the safe zone in wear maps and call for improvements in tool materials and coatings. We will then review the structure and surface properties of AM 3D printed metal parts. Economic, large scale finish machining of rough 3D printed metals will challenge current finish cutting routines and accelerate suitable changes in design and structure of cutting tools. The IIOT sensors will affect, primarily, machining of bulk materials. AM and 3D printed metals will speed up progress in finish cutting. We will discuss both cases with appropriate examples of tools and coatings for machining high temperature alloys, gray cast iron, and carbon composites.

2:40pm **B1-2-MoA-4 Overstoichiometric Transition Metal Nitride Films**, ***Zuzana Čiperová**, J Musil, Š Kos, M Jaroš,* European Centre of Excellence, University of West Bohemia, Czech Republic

Transition metal nitride films TMN_x with a high stoichiometry x = N/TM > 1 are advanced films with new unique properties; here TM are the transition metals such as Ti, Zr, Mo, Ta, Nb, W, etc. We report on their properties and formation by the reactive magnetron sputtering using dual hybrid magnetron. The principle of formation of overstoichiometric $TMN_{x>1}$ films is explained. Three $TMN_{x>1}$ coatings were investigated in detail: $ZrN_{x>1}$, $Ti(Al,V)N_{x>1}$ and TiN_2 dinitride films [1]. It was found that (1) the overstoichiometric $ZrN_{x>1}$ films are two-phase films with c-ZrN and o-Zr_3N_4 structure, (2) the overstoichiometric $Ti(Al,V)N_{x>1}$ and $TiN_{x>1}$ films are one-phase films with c-TiN structure, (3) the one-phase overstoichiometric $TMN_{x>1}$ nitride films can form the TMN_2 dinitride films such as TiN_2 dinitride, (4) the film stoichiometry x is a strong parameter which enables to control its mechanical properties and electric conductivity; for example, the electrical resistivity of the ZrN_x film varies with increasing x from well electrically conducting films with x ≤ 1 through the semi-conducting films with x ranging from 1 to ≤ 1.26 to non-conductive with x ≥ 1.3, and (5) the high base pressure p_0 ≥ 0.001 Pa in the deposition chamber after its evacuation strongly influences the structure and phase composition of sputtered nitride films.

Reference

[1] J.Musil, M.Jaroš, Š.Kos, R.Čerstvý, S.Haviar: Hard TiN_2 dinitride films prepared by magnetron sputtering, J. Vac. Sci. Technol. A 36(4) 2018, 040602-1 to -3.

3:00pm **B1-2-MoA-5 Introducing of New Hybrid LACS® Technology (Lateral ARC and Central Sputtering by Rotating Cathodes)**, ***Radek Zemlicka**, M Jílek (Sr.), M Jílek (Jr.), A Lümkemann, T Cselle, D Bloesch, V Krsek,* Platit AG, Switzerland

The flexible coating units which are able to work with ARC, sputtering and PACVD technologies are very suitable for the small and medium size enterprise. While the ARC brings the highest performance for cutting tools in cca 85% of the applications, the sputtering achieves very smooth surfaces for better chip evacuation and DLC coatings, made by PACVD, avoids build up edges at cutting sticky materials. The combination of these 3 technologies in one coating unit enables the use the advantages of all of them.

We would like to introduce the new LACS® technology (Lateral ARC and Central Sputtering by rotating cathodes) . The new feature of this hybrid technology is the combination of arc evaporated non-alloyed metallic (Ti,Al,Cr,W, etc) and magnetron sputtered ceramic (TiB2, B4C) targets, resp. cathodes.

It allows to deposit different high-performance coatings, like AlCrN/BN, AlTiN/BN, TiWN, TiCNWCC or TiB2. On the other hand, the supplementary electron injection provided by ARC discharge can improve the microstructure and performance of the plasma-enhanced magnetron sputtered coatings.

On the example of BN-containing coatings we would like to illustrate how is it possible to optimize mechanical parameters of the coating by tuning of the process parameters. We will also present industrial applications of the optimized coating.

3:20pm **B1-2-MoA-6 Edge-related Effects During Arc-PVD Deposition Processes**, ***Tim Krülle**, F Kaulfuss, O Zimmer, A Leson, C Leyens,* Fraunhofer Institute for Material and Beam Technology (IWS), Germany

The deposition of different coatings on shaped surfaces, such as on cutting tools (drills) faces problems especially on edges [1-2]. Normally the radii of such cutting edges are dramatically increased, if the coating thickness is increased. Also defects, damaging or resputtering of material on edges may occur. A multilayered coating based on AlCrSiN instead showed an interesting effect of edge sharpening during the deposition process. With this approach it would be possible to overcome the problem of edge rounding in PVD coating technology. The pictures below show different edge radii varying with the negative bias voltage and leading to a smaller edge radius as compared to the uncoated tools or tools without additional bias voltage [3].

Therefore the deposition process and important deposition parameters were investigated and the geometry of such edges was measured. Accompanying nano indentation hardness measurements give an overview of mechanical properties around the surface also in dependence of position and chemical composition of the coating.

REFERENCES:

[1] H. A. Jehn, “PVD coating of 3D parts studied with model samples”, Surface and Coating Technologies, Vol. 94-95, pp 232-236, 1997.

[2] J. Bohlmark, “Evaluation of arc-evaporated coatings on rounded surfaces and sharp edges”, Materials Science Forum, Vol. 681, pp 145-150, 2011.

[3]T. Krülle, FhI-IWS Dresden, Annual Report 2016, “Sharp edges thanks to coatings”, pp 106-107.

3:40pm **B1-2-MoA-7 Reactive Sputtering for Highly Oriented HfN Film Growth on Si(100) Substrate***, **Yu-Siang Fang**, K Chiu, H Do, L Chang,* National Chiao Tung University, Taiwan

Hafnium nitride have excellent properties such as high melting point, high hardness, low resistivity, which makes them potential in many technological fields. HfN have been investigated for diffusion barriers in semiconductor devices. $HfSi_2$ has been used for high temperature oxidation resistant coatings. However, there are no detailed studies for growth of epitaxial HfN/$HfSi_2$ films on Si substrate.

HfN films were grown on Si(100) substrates by reactive DC magnetron sputtering with Ar/N_2 gas mixture using a Hf target. The deposition was carried out by varying N_2 flow ratio and the power at 5 mTorr and 850℃.

XRD results with cross-sectional TEM/STEM show that low N_2 flow ratio favors the formation of the HfSi- interlayer between HfN and Si, while no HfSi-$_2$ diffraction peaks can be seen for high N_2 flow ratio of 12.5% . Also, increasing the applied power for sputtering results in the increase of the HfN peak intensity ratio of (200)/(111). Furthermore, it is shown that the orthorhombic $HfSi_2$ interlayer is in epitaxy with Si (100) and those (100) oriented HfN grains are found in epitaxy with both $HfSi_2$ and Si as well. The epitaxial relationship is HfN (100) [011] // $HfSi_2$ (020) [100] // Si (100) [011].

4:00pm **B1-2-MoA-8 Study of Orthorhombic $ZnSnN_2$ Fabricated using Zn–Sn_3N_4 Composition Spreads through Combinatorial Reactive Sputtering***, **Kao-Shuo Chang**,* National Cheng Kung University, Taiwan **INVITED**

The piezo-related properties of $ZnSnN_2$ (ZTN) will be presented. Natural Sn_3N_4 and Zn thickness gradients were fabricated using combinatorial magnetron sputtering to form Zn–Sn_3N_4 composition spreads to enhance the relative variation of the cation ratios and to promote the formation of orthorhombic ZTN. Sn_3N_4 and the single crystallinity of orthorhombic ($Pna2_1$) ZTN nanocolumn arrays growing along the [001] direction were confirmed by locked-coupled XRD and TEM. The diffusion and variation of the atomic binding state of constituent elements were studied using SIMS depth profiling and XPS. The band gap of ZTN was estimated to be approximately 2.0 eV from a UV–vis measurement. The piezotronic and piezophototronic effects of ZTN were ascertained and illustrated by the Schottky barrier height variations. Excellent piezophotocatalysis was also observed, which was attributed to the reduced recombination of the photogenerated e^-–h^+ pairs. In addition, $^{\bullet}O_2^-$ radicals were predominate in the photodecomposition process.

4:40pm **B1-2-MoA-10 Angular Resolved Mass-energy Analyses of Species Emitted from a d.c. Magnetron Sputtered NiW-target***, **Martin Rausch**,* Montanuniversität Leoben, Austria*; S Mraz, J Schneider,* RWTH Aachen University, Germany*; J Winkler,* Plansee SE, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

Advanced thin film applications e.g. in thin film transistors, electrochromic glasses or hard coatings frequently require sputtering targets consisting of multiple chemical elements with large differences in atomic weight. An understanding of sputtering, gas-phase transport and deposition characteristics of thin film systems deposited from such multi-element targets becomes increasingly important. For the previously investigated system $Mo_{0.70}Al_{0.20}Ti_{0.10}$ (m_{Mo}=95.95 u, m_{Al}=26.98 u, m_{Ti}=47.87 u) it was shown that not only (*i*) element-specific differences in sputter yield and initial emission angle, but also the (*ii*) transport of sputtered particles through the gas, accompanying (*iii*) collisions with background gas atoms with concomitant energy loss of sputtered particles, and (*iv*) the interaction of transmitted energetic particles with the surface of the growing thin film, such as preferential re-sputtering, will have an impact on the film morphology as well as the chemical composition of the films [1]. For the system NiW, which is used for the deposition of electrochromic thin films, the difference in atomic weight of the target constituents is significant (m_{Ni}= 58.69 u, m_W=183.84 u), making it an ideal model system to study the mechanisms mentioned above. Since it was concluded in [1] that the initial emission angle and the corresponding energy of sputtered atoms have a substantial impact on differences in morphology and chemical composition of the films, a 180 ° turnable magnetron with a mass-energy analyzer mounted opposite the target at a distance of 80 mm was used to d.c. sputter a $Ni_{0.80}W_{0.20}$ target at Ar pressures ranging from 0.01 to 1 Pa. This setup allowed measuring both, flux and energy of sputtered Ni and W, but also of Ar reflected from the target and ionized in the plasma, at any given angle between 0 and 90° with respect to the target normal. Subsequent thin film deposition with a spherical-shell substrate holder covering the examined angles at deposition positions from 0 to 80 ° in 10 ° steps allowed correlating the mass-energy measurements with thin film growth experiments. Film thickness measurements, structure and composition analysis yielded insights into the relation between emission angle and energy of transmitted particles and angular dependent structure and composition evolution of the deposited films.

[1] M. Rausch, M. Pavlovič, P. Kreiml, M.J. Cordill, J. Winkler, C. Mitterer, Applied Surface Science 455 (2018) 1029–1036.

5:00pm **B1-2-MoA-11 Effect Produced by Architecture of Nanolayer Composite Coatings Deposited with Filtered Cathodic Vacuum Arc Deposition (FCVAD) Technology on their Mechanical and Performance Properties***, **Alexey Vereschaka**, S Grigoriev,* Mstu Stankin, Russian Federation*; N Sitnikov,* National Research Nuclear University MEPhI, Russian Federation*; N Andreev,* National University of Science and Technology “MISiS”, Russian Federation

The paper deals with the technique of forming coatings with nanolayer structure, including nanolayers (formed due to rotation of a turntable in a chamber) and subnanolayers (formed due to planetary rotation of rigging elements). The SEM and TEM methods were used to study the coating structure. In particular, the Ti-TiN-(Ti,Al,Si)N, Zr-ZrN-(Zr,Cr,Al,Si)N and ZrNb-ZrNbN-(Zr,Nb,Cr,Al,Si)N coatings were considered. The thickness of binary nanolayers in the coatings under study was 20-70 nm, while the thickness of subnanolayers was 2-20 nm. The study also considered the mechanism of coating failure in scratch testing, depending on thickness of nanolayers and subnanolayers. The investigation found significant differences in the value of the critical failure force L_{C2} and the pattern of failure, depending on the thickness of coating nanolayers. The change in the value of adhesion component of the friction coefficient for samples with the coatings under study within the temperature range of 20-1000°C was studied. Cutting tests were conducted for carbide tools with the coatings under study in turning steel C45 at f = 0.25 mm/rev, a_p = 1.0 mm, v_c = 200-350 m/min. The patterns of wear and failure for coated tools were studied, as well as oxidation and diffusion processes. As a result of the conducted studies, a range of values for optimal thickness of nanolayers was determined to make it possible to increase the cutting speed by 25-30% while maintaining the tool life period and the high quality of the machined surface.

5:20pm **B1-2-MoA-12 Effects of Nitrogen Flow Rate and Substrate Bias on Structure and Properties of Molybdenum Nitride Thin Film***, **Cho-Cheng Chou**, J Huang,* National Tsing Hua University, Taiwan

Molybdenum nitride is well known as a wear resistant material with high hardness, which has three different thermodynamic stable crystal structures, tetragonal β-Mo_2N, cubic γ-Mo_2N, and hexagonal δ-MoN, among which γ-Mo_2N possesses the best mechanical performance. However, there is little research on the relationship of β- and γ-Mo_2N transformation. The purposes of this study are to investigate the order-disorder phase transformation of $Mo_{2-x}N$ thin film by controlling the deposition parameters, including nitrogen flow rate and substrate bias, and to explore the relationship between mechanical properties of different phases. The $Mo_{2-x}N$ thin films were prepared on Si substrate using unbalanced magnetron sputtering with different nitrogen flow rate and substrate bias. After deposition, the film hardness and crystal orientation were characterized by nanoindentation and X-ray diffraction, respectively. The residual stress of the thin film was measured using laser curvature and XRD $\cos^2\alpha\sin^2\psi$ methods, which may affect hardness and adhesion of the thin film. The microstructure was observed by scanning electron microscopy and atomic force microscopy. The electrical resistivity and chemical compositions were measured by a 4-point probe and X-ray photoelectron spectroscopy. Based on the experimental results, the mechanical properties were correlated to structure of the thin films.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B3-2-MoA

Deposition Technologies and Applications for Diamond-like Coatings II

Moderator: Frank Papa, Gencoa

1:40pm **B3-2-MoA-1 Transfer of DLC Coating Processes between Different Coating Machines Assisted by Plasma Simulation**, ***Marcus Günther**, O Schmidt, W Dobrygin, G Schütze,* Robert Bosch GmbH, Germany

Hydrogenated amorphous carbon films (a-C:H) as a kind of diamond-like carbon (DLC) coatings combine unique optical, electrical and mechanical properties, resulting in numerous industrialized applications. These plasma coatings are continuously of high interest for research and industry because of the possibility to adjust their layer properties in a wide range by varying the deposition conditions like pressure, temperature or bias voltage. DLC films are widely used in the automotive industry due to their unique tribological properties, e.g. as an enabler for modern fuel injection equipment.

Important goals of a modern flexible industrial production especially for automotive mass production are the realization of good adhesion, functionality of the layer system and the fundamental control of the deposition process regardless of the kind of coating machine and coated component geometry. The combination of plasma simulation, coating experiments and plasma diagnostics enables the monitored deposition of hydrogenated amorphous carbon films and the prediction of the resulting layer properties, e.g. hardness, intrinsic stress or hydrogen content.

The study will present a global model for acetylene and argon plasmas to support the process development for the functional a-C:H-layer and the process transfer between different coating machines for the industrialized deposition to guarantee consistent a-C:H-layer quality. With the presented simulation, it is possible to calculate all partial pressures of reaction products, relevant plasma parameters and particle fluxes. By transferring all relevant machine parameters (e.g. bias voltage, gas flow, …) into only one main virtual parameter, the energy per deposited carbon atom, it is possible to compare and generically predict the coating quality of various coating machines with different chamber sizes and vacuum pumping systems.

2:00pm **B3-2-MoA-2 Stress-Free ta-C Industrially Deposited by PLD for High Performance Stamping Applications: Results and Challenges of 1st Production Year**, ***Martin Hess**,* Fritz Stepper GmbH & Co. KG, Deutschland, Germany*; S Weißmantel, R Bertram,* Hochschule Mittweida University of Applied Sciences, Germany

At the 45th ICMCTF conference, we presented PLD as a new system technology for the production of stress-free ta-C coatings which are summarizable by a very high hardness of over 60 GPa while retaining the common layer thicknesses of 3 to 4 µm (which are previously and still used for our PVD tool coatings coated by Sputter- and Arc-PVD). Among other things PLD allowed us to deposit ta-C without changing tool drawings (which are proven over many years) if we mix ta-C- with PVD coatings in our high performance progressive die tools. Moreover we can avoid egg shell effects, which may be a drawback if very hard but relatively thin (ca. 1 µm) coatings are used in highly stressed applications.

PLD ta-C achieves, compared to so far used PVD coatings, almost double hardness in combination with a significantly artifact less surface. As a result the abrasion resistance against some stamping strips and active component lifetime are boosted by a magnitude and more – which saves tool cost and press down time. As presented in 2018 our daily quantities and tool sizes are relatively small, even for compliance with compact PVD systems, we decided to design a PLD system dedicated to our requirements for our final products: Complex modular die tools (with more than 1000 coated active elements) which are able to produce multi-millions of electrical contacts in a 24/7 operation without any maintenance.

In the meantime our PLD coating system has been in operation for more than one year. Driven by demanding applications, such as Si-containing high-strength bronze, stainless steel, the ta-C coatings became smarter (e.g. integrated run-in layer, tailored hardness and Young's modulus, etc.) and more performing. Significant progress was e. g. also made regarding the coating of die cavities.

The purpose of the present contribution is to introduce latest developments of ta-C produced by PLD. For this purpose, relevant mechanical properties as well as new successful applications will be presented.

2:20pm **B3-2-MoA-3 Hollow Cathode Discharges for Rapid DLC**, ***Thomas Casserly**, S Gennaro, F Papa, A Tudhope,* Duralar Technologies, USA**INVITED**

The application of Diamond Like Carbon coatings has been limited by the cost and time required to deploy the coating. Hollow cathode discharges are characterized by their high ion densities and hot oscillating electrons capable of multiple ionization events. Through harnessing the power of hollow cathode discharges internal surfaces of conductive hollow articles can be coated rapidly with DLC (and other materials). This internal deposition technology enables numerous applications of DLC for low wear and low friction in engine cylinders, actuators, hydraulic cylinders, and more as well as anti-wear, anti-fouling and anti-corrosion applications in upstream oil and gas and adjacent markets. Deposition rates in excess of 5 µm per minute have been achieved for specific geometries allowing for cost effective deployment of advanced coatings. This high rate hollow cathode deposition technology has been extended to coat external surfaces as well; initially, for shafts, plungers, and other cylindrical objects through the application of annular hollow cathode geometries. Using a similar approach designed for high throughput, the deposition technology has been developed to coat the external and internal surfaces of complex objects with applications in armaments, sporting, and automotive components, as well as functional decorative coatings for consumer products. The high deposition rates and throughput afforded by hollow cathode discharge technology greatly reduces the cost of deploying advanced DLC coatings and enables a diverse set of applications.

3:00pm **B3-2-MoA-5 Hard Cr-doped DLC Coatings Deposited by Low-frequency HiPIMS with Enhanced Tribomechanical Behavior at High Temperature**, ***José Antonio Santiago Varela**,* PVT Plasma und Vakuum Technik GmbH, Germany*; I Fernandez,* Nano4Energy SL, Spain*; A Wennberg,* Nano4Energy, Spain*; M Monclus, J Molina Aldareguia,* IMDEA Materials*; V Bellido-Gonzalez,* Gencoa Ltd, UK*; C Rojas, J Sanchez Lopez,* ICMSe CSIC, Spain*; R Gonzalez Arrabal,* Universidad Politécnica de Madrid, Spain*; N Dams, H Gabriel,* PVT Plasma und Vakuum Technik GmbH, Germany

Diamond-like Carbon (DLC) coatings have been recognized as one of the most valuable engineering materials for various industrial applications including manufacturing, transportation, biomedical and microelectronics. Among its many properties, DLC stands out for a good frictional behaviour combined with high surface hardness, offering an elevated protection against abrasive wear. Nevertheless, a factor limiting the widespread application of DLC coatings is their thermal stability. DLC is very temperature-sensitive since its sp^3-sp^2 structure undergoes a graphitization process at high temperatures that deteriorates both hardness and coefficient of friction. In order to overcome this limitation, new ways to modify DLC coatings for acceptable high temperature performance have been explored. In this work, we investigated the deposition of hard DLC coatings doped with Cr using HiPIMS technique at industrial scale. Extraordinary highly ionized plasma discharges were obtained during chromium and carbon codeposition at low HiPIMS frequencies. The high ion energy bombardment at low HiPIMS frequencies allowed doping with Cr the DLC structure while reaching high sp^3 contents. EELS spectroscopy was used to evaluate sp^3 content and Raman was used for sp^2 structural characterization of the films. Enhanced mechanical properties (hardness up to 35 GPa) were observed with nanoindentation for Cr-doped DLC at low frequencies. High temperature nanoindentation tests were also performed from room temperature to 450ºC in order to evaluate the evolution of hardness and Young Modulus with temperature. The results confirm that the mechanical properties at high temperature mainly depend on the sp^3 content. Tribological tests were carried out in air from room temperature to 250ºC. Cr-doped DLC coatings showed lower friction and wear compared to pure DLC. The increased toughness that Cr provides to the carbon matrix together with a high sp^3 bonding structure obtained with low frequency HiPIMS deposition improves the stability of DLC coatings for high temperature applications.

3:40pm **B3-2-MoA-7 Effect of Pulse Shape and Plasma Composition (Ar + Ne) on the Properties of Hard DLC Films Deposited by HiPIMS: Correlation with Substrate Ion Fluxes**, ***João Oliveira**, F Ferreira, R Serra,* University of Coimbra, Portugal*; T Kubart,* Uppsala University, Angstrom Laboratory, Sweden*; C Vitelaru,* National Institute for Optoelectronics, Romania*; A Cavaleiro,* University of Coimbra, Portugal

High Power Impulse Magnetron Sputtering (HiPIMS) has been under consideration for hard Diamond Like Carbon (DLC) thin films deposition in recent years. The major driver to use HiPIMS is the possibility of C ions formation in the plasma and their subsequent subplantation upon substrate biasing to promote the formation of sp^3 bonds in a similar way to

ARC deposition. However, the low electron impact ionization cross-section of C limits the C^+/C ratio in HiPIMS plasmas to some few percent (~ 5 %). Adding Ne to the discharge gas allows increasing the electron temperature of the plasma and, thus, increasing the C ionization fraction. On the other hand, the use of short pulse on-times (<10 µs) together with high target voltages (>1 kV) has been reported to result in large target current densities.

In this work the effect of adding Ne to a pure Ar discharge and the use of different HiPIMS pulse shapes are investigated. DLC films were deposited by HiPIMS using two different power supplies providing HiPIMS pulses with different temporal duration and peak voltages. The structural and mechanical properties of the DLC films were evaluated by micro-Raman Spectroscopy and Nanoindentation, respectively. The tribological behavior of the DLC films was evaluated by pin-on-disk tests in ambient atmosphere (room temperature and ~ 40% relative humidity). The friction coefficients of the DLC films were obtained by averaging over last 1000 m of the sliding tests. The specific wear rate (k) of the DLC films was calculated from the cross-section profiles of the wear tracks. Additionally, the time-resolved substrate current densities (SCDs) were measured using a flat probe mounted at the substrate position. The measured Ion Saturation Currents (ISCs) were correlated to the structural, mechanical and tribological properties of DLC films.

Adding Ne to the HiPIMS plasma results in a significant increase of both the sp^3 content and the hardness (> 20 GPa) of the DLC films while their fiction coefficient remains within the range typical of DLC films tested under relatively humid conditions (< 0.2). The specific wear rate of the DLC films decreases with Ne addition down to a minimum value of 4 $x10^{-17}$ m^3/Nm.

4:00pm **B3-2-MoA-8 The Comparison of Deposition Processes, Composition and Properties of Hydrogenated W-C:H Coatings Prepared by Different Sputtering Techniques***, **Frantisek Lofaj**, M Kabatova, L Kvetkova,* Institute of Materials Research of SAS, Slovakia*; J Dobrovodsky,* ATRI, Slovakia

The work reviews the processes and subsequent mechanical and tribological properties of hybrid PVD/PECVD sputtering during deposition of hydrogenated W-C:H coatings prepared by High Power Impulse Magnetron Sputtering (HiPIMS) and High Target Utilization Sputtering (HiTUS) as a function of acetylene and hydrogen additions in the Ar atmosphere. The results are compared with those from analogous coatings deposited by conventional direct current magnetron sputtering. TEM observations revealed that a transition from nanocrystalline WC_{1-x} to nanocomposite and amorphous structure occured with the increase of acetylene addition nin all coatings but at different acetylene contents. The concentrations of carbon and hydrogen in the studied coatings measured by Rutherford Backscattering (RBS) and Elastic Recoil Detection Analysis (ERDA) methods depended on the amount of acetylene and hydrogen addition but also on the applied technique. The obtained results were analyzed and the main differences in the possible growth mechanisms between DCMS and HiPIMS were discussed within the von Keudell model for a-C:H growth. The increase of free carbon content in HiTUS W-C:H coatings when C_2H_2 was added resulted to a degradation of indentation hardness and indentation modulus similarly as in DCMS coating. However, almost no degradation was observed in HiPIMS coatings. Low coefficients of friction in HiTUS and DCMS coatings were attributed to the formation of lubricious tribolayer whereas uniform structure was considered to be a property controlling parameter in HiPIMS coatings. The main advantage of HiPIMS compared to HiTUS and DCMS coatings includes lower coefficients of friction at higher hardness values.

4:20pm **B3-2-MoA-9 The Mechanism of Graphite Nucleation in Amorphous Carbon Films Deposited with the Condition of Energetic Bombardment and High Temperature***, **Di Zhang**, P Yi, L Peng, X Lai,* Shanghai Jiaotong University, China

Amorphous carbon (a-C) films exhibit many properties that make them attractive for applications in coating technology. The property of a-C films closely depends on their microscopic structures and a-C films with a graphite-like structure may exhibit high electrical conductivity and excellent corrosion resistance, mainly due to the nucleation of graphite nanocrystals observed in a-C matrix. However, the mechanism of graphite nucleation remains unclear. This work aims to develop a fundamental understanding of the graphite nucleation in a-C films deposited with energetic bombardment and high temperatures. Our experiments revealed that different sizes of graphite nanocrystals were observed in a-C films produced by applying varying deposition bias voltages and temperatures, thus leading to a different durability under the a typical corrosive environment of proton exchange membrane fuel cells. Moreover, we developed an atomistic model to simulate the nucleation of graphite nanocrystals in a-C films using Molecular Dynamics and Monte Carlo methods. Investigations on the structural properties of the atomistic model provide fresh insights into the microscopic structure of graphite-like a-C films.

Hard Coating and Vapor Deposition Technologies
Room Golden West - Session B1-3-TuM

PVD Coatings and Technologies III

Moderators: Frank Kaulfuss, Fraunhofer Institute for Material and Beam Technology (IWS), **Jyh-Ming Ting**, National Cheng Kung University, **Qi Yang**, National Research Council of Canada

8:00am **B1-3-TuM-1 PVD-AlTiN with High Al Content – How to Overcome the "Magic" 67%-Limit**, ***Fred Fietzke***, *T Modes, O Zywitzki,* Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Germany

Since first investigations in the 1980's, TiAlN has become the most widespread coating material for wear protection in cutting applications. For the use at high temperatures, its corrosion resistance can be further improved by increasing the aluminum content in the cubic rock salt (Ti,Al)N phase. However, the solubility of Al in this phase is limited, and above a certain threshold AlN with hexagonal wurtzite structure is formed in addition. This leads to a sharp drop of hardness and a general deterioration of wear resistance.

Whereas the application of CVD techniques allows the deposition of single phase cubic $Al_xTi_{1-x}N$ layers with x > 0.8, the accepted state of the art for PVD is a maximum x-value of 0.67.

To find out how the effective maximum-x-value depends on the deposition conditions, a co-sputtering approach was used and compositionally graded layers with increasing Al content in growth direction were deposited. By FE-SEM investigation of cross sections in crystal orientation contrast it could be shown that the microstructure is changed at a certain depth, from large columnar crystallites with lateral dimensions of about 60 nm to a nanocrystalline structure with globulitic crystallites in the range of 10 nm.

XRD measurements showed that the initially deposited columnar structure is single-phase cubic, whereas the nanocrystalline layer arising on top is hexagonal with wurtzite structure. Hardness measurements by nanoindentation gave results up to 40 GPa for the lower and around 20 GPa for the upper layer. The depth profiles of chemical composition were determined by GD-OES. The results show that the layers are stoichiometric and exhibit aluminum gradients of different slope.

The location of the phase change from cubic to hexagonal could be affected by deposition conditions like pressure, temperature, and bias voltage. By optimization of the process parameters, it was possible to shift the phase transformation from x-values of 0.67 to 0.75.

8:20am **B1-3-TuM-2 PVD Methods and Coatings for Protection of Aero Engine Components**, ***Uwe Schulz***, *R Naraparaju, R Braun, N Laska,* German Aerospace Center (DLR), Germany **INVITED**

Advanced aero engines aim at reduced specific fuel consumption and increased thrust-to-weight ratio. This ultimately calls for materials with increased high temperature capability and lightweight components that are pushed to its limits. Usage of coatings offers the potential to prolong lifetime, to increase operating temperatures, and to protect turbine components. Several PVD coating techniques that are used to protect turbine parts will be presented.

Thermal barrier coatings (TBCs) are applied to increase lifetime and efficiency of turbine blades and vanes in aero-engines and land-based gas turbines by reducing the average metal temperature and mitigating the detrimental effects of hot spots. The presentation highlights the interplay between processing, microstructure, and lifetime of the coatings that are produced by electron beam-physical vapor deposition (EB-PVD. Those coatings possess a superior strain and thermo-shock tolerance due to their columnar microstructure. The influence of substrate material, bond coat composition, and top coat composition is discussed. New topcoat chemistries have been developed that offer low thermal conductivity, improved sinter resistance, higher phase stability, and especially enhanced resistance against degradation by volcanic ash and calcium-magnesium alumino-silicate (CMAS) deposits that are ingested in aero-engines during the flight. The presentation provides results on several new TBCs, especially their behavior under the influence of deposits and under thermo-cyclic loading.

Gamma-TiAl based alloys are attractive light-weight materials for high temperature applications in automotive and aero engines. However, their oxidation resistance is poor at temperatures above 800°C. To improve the oxidation behavior of TiAl components, the use of protective coatings is a suitable method. Furthermore, the application of TBCs on TiAl would allow a further increase in operating temperature of internally cooled components. In the presentation several alumina forming coatings such as PtAl, Ti-Al-Cr based coatings and TBCs of yttria partially stabilized zirconia (YSZ) are discussed. They were deposited on gamma-TiAl alloys using magnetron sputtering and electron-beam physical vapour deposition, respectively. The oxidation behavior of the protective layers and the lifetime of the TBC systems are presented in the temperature range between 900 and 1000°C performing thermal cyclic tests.

PVD methods are also capable to protect CFRPs against erosion which is another damaging effect in aero-engines. Here multilayers of metallic and hard coatings are favored to effectively protect the underlying material.

9:00am **B1-3-TuM-4 High-temperature Nanoindentation and Microcantilever Deflection Tests of CrAlN and CrAlSiN Hard Coatings**, ***Aljaž Drnovšek***, Montanuniversität Leoben, Austria*; H Vo,* University of California Berkeley, USA*; A Xia, M Rebelo de Figueiredo,* Montanuniversität Leoben, Austria*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; S Vachhani,* Bruker Nano Surfaces, Germany*; P Hosemann,* University of Californa at Berkeley, USA*; R Franz,* Montanuniversität Leoben, Austria

Mechanical properties of protective coatings are commonly determined by nanoindentation methods. The development of nanoindentation in recent years led to new ex-situ and in-situ systems that are capable of measuring mechanical properties such as hardness, elastic modulus and fracture toughness at high temperatures (HT). For hard protective coatings it is of paramount value to gain knowledge of their mechanical properties close to the real operation temperature.

In the current work, we tested two magnetron sputter deposited coatings that are widely used in industrial cutting applications, namely CrAlN and CrAlSiN. Although the coatings consist of similar elements, the addition of Si interrupts the columnar growth of CrAlN coatings resulting in a nanocomposite composed of CrAl(Si)N grains surrounded by an amorphous SiN_x grain boundary phase. We measured their HT hardness and elastic modulus up to 700°C in steps of 100°C. The hardness value reduced from 30 GPa and 36 GPa for CrAlN and CrAlSiN, respectively, by approximately 2 GPa per temperature step. In contrast to a gradual decrease of hardness over the whole temperature range for CrAlN, the hardness of CrAlSiN revealed only minor changes at temperatures exceeding 500 °C. The HT fracture toughness was measured by microcantilever deflection using in-situ nanoindentation. These measurements were conducted in a similar way as the hardness measurements, up to 700°C in 100°C steps. We found that the trend is similar to the HT hardness results with CrAlSiN exhibiting a slightly better performance.

This data set is intended to serve as a first step towards a more comprehensive understanding of the HT mechanical properties of hard coatings which is vital for their further development and improvement for use in HT applications.

9:20am **B1-3-TuM-5 On Crystallization and Oxidation Behavior of $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ Thin-film Metallic Glasses Compared to a Crystalline $Zr_{54}Cu_{46}$ Thin-film Alloy**, ***Michaela Kotrlová***, *M Zítek, P Zeman,* University of West Bohemia, Czech Republic

Zr- and Cu-based metallic glasses are one of the most studied systems because of their high crystallization temperature and a wide supercooled liquid region. Their unique properties make them attractive for miscellaneous applications. An important prerequisite to use them in industry is their ability to resist an oxidizing environment at elevated temperatures.

Therefore, this work is focused on the investigation of the crystallization and oxidation behavior of $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses and on the comparison of their oxidation behavior with that of a crystalline $Zr_{54}Cu_{46}$ thin-film alloy. The amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ thin-film metallic glasses were prepared by non-reactive magnetron co-sputtering of Zr, Hf and Cu in pure argon. The magnetrons with the Zr and Hf targets were operated in dc regimes while the magnetron with the Cu target in high-power impulse regime. Several as-deposited $Zr_{54}Cu_{46}$ films were post-annealed in high vacuum to create a crystalline thin-film alloy of the identical composition. The non-isothermal crystallization behavior of the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films and the effect of a substitution of Hf for Zr on the crystallization process were studied by differential scanning calorimetry. The oxidation behavior of the amorphous and crystalline $Zr_{54}Cu_{46}$, and amorphous $Zr_{27}Hf_{27}Cu_{46}$ films was investigated by thermogravimetric analysis.

The results showed that the $Zr_{54}Cu_{46}$ film crystallized at a lower temperature (≈ 422°C) and in two successive steps in contrast to the $Zr_{27}Hf_{27}Cu_{46}$ film (≈ 477°C). The activation energy of the $Zr_{27}Hf_{27}Cu_{46}$ film was higher for all conversion fractions, which indicates that the substitution of Hf for Zr enhanced the thermal stability of the glassy state. Dynamical thermogravimetric curves revealed that the onset of the oxidation of the amorphous $Zr_{54}Cu_{46}$ film (≈ 475°C) was shifted by about 120°C to a higher temperature than for the crystalline $Zr_{54}Cu_{46}$ film. Moreover, the substitution of Hf for Zr shifted the onset of the oxidation to an even higher temperature (≈ 550°C). As for oxidation kinetics, all isothermal thermogravimetric curves in the temperature range from 400 to 575°C obeyed the parabolic law. The activation energy of the oxidation process was 112, 143 and 208 kJ/mol for the crystalline $Zr_{54}Cu_{46}$ film, and the amorphous $Zr_{54}Cu_{46}$ and $Zr_{27}Hf_{27}Cu_{46}$ films, respectively. The highest activation energy for the $Zr_{27}Hf_{27}Cu_{46}$ film indicates that the most protective oxide layer was formed on the surface of this film.

9:40am **B1-3-TuM-6 On the Origin of Multilayered Structure of W-B-C Coating Prepared by Non-Reactive Magnetron Sputtering from a Single Segmented Target***, **Michael Kroker**, P Soucek, M Fekete, L Zabransky, V Bursikova,* Masaryk University, Brno, Czech Republic*; P Zikan, A Obrusnik,* Plasma Solve, Brno, Czech Republic*; Z Czigany, K Balazsi,* Hungarian Academy of Sciences, Hungary*; P Vasina,* Masaryk University, Brno, Czech Republic

Machining tools are routinely coated with thin films to enhance their performance and durability. Nowadays used hard protective coatings exhibit high hardness and high stiffness; however, these positive features are often accompanied by negative brittle deformation behaviour, which facilitates formation and spreading of cracks. This leads to a premature degradation of the coated tool. A solution would be to prepare coatings simultaneously exhibiting high hardness together with enhanced ductility. Recently, there has been an increased interest in crystalline metal-boron-carbon based coatings [1] with X2BC stoichiometry which is inherently nanolaminated within the unit cell. According to the ab-initio models [1], these materials should exhibit an unusual combination of high stiffness and moderate ductility. A systematic theoretical study revealed that the nanolaminates with X = W should exhibit the best mechanical properties [1] making them the best candidates for experimental synthesis. Thus W-B-C coatings were sputter deposited in non-reactive atmosphere onto substrates performing a planetary motion around a central rotating cylindrical target composed from boron-carbide, tungsten and graphite segments in an industrial scaled deposition system of company SHM, Sumperk, Czech Republic. The coatings were deposited at the temperature of 450 °C and bias of -100 V by direct current magnetron sputtering. The SEM and TEM cross-section view revealed the presence of multilayered structure. The pattern of the multilayered structure was dependent on the type of planetary rotation around the central target. According to EDX and GDOES, the multilayered structure consisted of tungsten-rich layers alternating with boron- and carbon-rich layers. The whole structure consisted of thin layers with the thickness not exceeding 15 nm. The number of the multilayers was correlated with the number of the revolutions the sample performed during the deposition process. The multilayered structure was attributed to different transport pathways of heavy (W) and light (C and B) atoms sputtered from the target and scattered by working gas. 3D DSMC model was developed to explain the transport of sputtered atoms. The model is using the experiment geometry and initial velocities of sputtered particles calculated by TRIM. Results obtained with this model are in good agreement with experiment.

[1]H. Bolvardi, J. Emmerlich, M. to Baben, J, von Appen, R. Dronskowski, J.M. Schneider, Systematic study on the electronic structure and mechanical properties of X BC (X = Mo, Ti, V, Zr, Nb, Hf, Ta and W), J. Phys.-Condens. Mat. 25 (2013) 045501.

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

Properties and Characterization of Hard Coatings and Surfaces I

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

8:20am **B4-1-TuM-2 Preparation and Characterization of Hard and Tough Coatings of Ion-assisted Co-sputtered Transition Metal Borides***, **Ming-Show Wong**,* National Dong Hwa University, Taiwan **INVITED**

Transition metal borides (TMeB) are frequently explored around the globe due to their superior mechanical, tribological, electrical properties and chemical stability. Titanium diboride (TiB_2) is the most promising and explored material, while the other TMeBs like zirconium and tantalum diboride (ZrB_2 and TaB_2) sharing the same crystal structure and common properties receive relatively low attention. TMeBs are usually hard but brittle, which limit their wide spread applications. To prepare both hard and tough coatings of TMeBs, various approaches have been taken including doping, solid solution, ion bombardment, and multilayer. In the Ti-Zr-Ta-B system, ceramic-meal composites like TiB_2-Zr, ZrB_2-Ta composites, $TiZrB_2$ and $TiTaB_2$ solid solution and TiB_2/ZrB_2 multilayer films were explored by co-sputtering the corresponding TMeB ceramic target and/or metal target under various substrate bias voltages. Appropriate doping, solid solution, multilayer and ion bombardment could result in textured films with preferred structure with enhanced properties. Ion bombardment on the growing film greatly affects the crystal preferred orientation, crystallinity, composition, grain size, surface roughness, stress, toughness and hardness of the TMeB films. The change in target power ratio for solid solution films and in bilayer thickness for multilayer all affected the structure of the obtained films influencing intensity of texture, distortion of crystal lattice and residual stress. Superhard and tough films with hardness over 50 GPa and fracture toughness over 3 $MPa.m^{1/2}$ have been achieved consistently

9:00am **B4-1-TuM-4 Strategy for Increasing Both Hardness and Toughness in Transition-metal Diboride Thin Films***, B Bakhit,* Linköping Univ., IFM, Thin Film Physics Div., Sweden*; I Petrov,* University of Illinois, USA, Linköping University, Sweden, USA*; J Greene,* University of Illinois, USA, Linköping University, Sweden, National Taiwan Univ. Science & Technology, Taiwan*; L Hultman, J Lu, J Rosén, G Greczynski, **Naureen Ghafoor**,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

Refractory transition-metal (TM) diborides exhibit inherent hardness. However, this is not always sufficient to prevent failure in applications involving high mechanical and thermal stresses, since hardness is typically accompanied by brittleness leading to crack formation and propagation. Toughness, the combination of hardness and ductility, is required to avoid brittle fracture. Here, we propose a strategy for enhancing *both* the hardness and ductility of ZrB_2 thin films, selected as a model TM diboride, grown by hybrid high-power pulsed and dc magnetron co-sputtering (HiPIMS/DCMS) in pure Ar. A Ta target operated in HiPIMS mode, with a substrate bias synchronized to metal-rich portions of HiPIMS pulses, supplies energetic Ta ions to the growing film, while a compound ZrB_2 target operated in DCMS mode provides a continuous flux of Zr and B atoms. The average power P_{Ta} applied to the HiPIMS Ta target, and the HiPIMS pulse frequency, are varied from 0 to 1800 W (300 Hz) in increments of 600 W. All other deposition parameters are maintained constant. The resulting boron-to-metal ratio, y = B/(Zr + Ta), in as-deposited $Zr_{1-x}Ta_xB_y$ films continuously decreases from 2.4 to 1.5 as P_{Ta} is increased from 0 to 1800 W, while x increases from 0 to 0.3. A combination of XTEM, analytical Z-contrast STEM, EELS, EDX, and XRD analyses, reveal that all films have the AlB_2 hexagonal crystal structure with a columnar microstructure. Layers with x < 0.2 have B-rich column boundaries, whereas those with x ≥ 0.2 have Ta-rich column boundaries. This microstructural transition results in an increase of ~20% in hardness, from 35 to 42 GPa, with a simultaneous increase of ~50% in the nanoindentation toughness, from 3.5 to 5.2 MPa√m.

9:20am **B4-1-TuM-5 Tribocorrosion Resistance of Borided ASTM F1537 Alloy**, *I Campos-Silva,* ***Angel Manuel Delgado-Brito,*** Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; J Oseguera-Peña,* Tecnologico de Monterrey-CEM, México*; J Martinez-Trinidad,* Instituto Politecnico Nacional, Grupo Ingenieria de Superficies, México*; R Perez Pasten-Borja,* Instituto Politecnico Nacional, SEPI ENCB, Mexico*; D Lopez-Suero,* Instituto Politecnico Nacional, Grupo Ingenieria de Superficies, México*; A Mojica-Villegas,* Instituto Politecnico Nacional, ENCB, México

New results about the tribocorrosion resistance of borided ASTM F1537 alloy, immersed in Hanks' solution were estimated in this study. A CoB-Co_2B layer, with around 30 microns of thickness, was obtained at the surface of the alloy using the powder-pack boriding process at 1273 K with 6 h of exposure. Before the tribocorrosion tests, indentation properties such as hardness, fracture toughness, the residual stresses were obtained at the surface of the borided cobalt alloy. Otherwise, the tribocorrosion tests were carried out in a linear reciprocating tribometer coupled with a standard three-electrode electrochemical cell, in which a 5 mm diameter alumina ball worn the specimen surface immersed in Hanks' solution. A constant load of 20 N was applied over the surface of the material considering a stroke length of 2.5 m, and a total sliding distance of 100 m.

To estimate the material loss due to wear only, corrosion only, and the component due to the wear-corrosion synergism, four tests were conducted according to the ASTM G119 procedure: two wear tests, a) one in which the total material loss due to wear and corrosion (T) was estimated, b) another performed at 1 V cathodic of the open circuit to eliminate the corrosion component, defined as W_o. In the case of the corrosion tests, c) the polarization resistance was evaluated (C_o), without the influence of the wear component, and finally, d) the influence of the wear component in the corrosion behavior (C_w) was estimated. In all the cases, and to evaluate the influence of the boride layer developed at the surface of the ASTM F175 alloy, the experimental procedure was also established on the untreated material.

The results established that the presence of CoB-Co_2B layer decreases the total material loss due to wear and corrosion synergy compared to the untreated material. For the untreated material, the 62 % of the material loss was attributed to the wear-corrosion synergism in comparison with the 38 % estimated for the borided cobalt alloy. Finally, the influence of wear affected in greater extent than corrosion in the untreated material, while for the borided alloy the interaction between corrosion and wear was equal.

9:40am **B4-1-TuM-6 Corrosion Behavior of TiAlSiN Doped with Ag Coating Deposited by Co-sputtering in Physiological Fluids**, ***Alvaro Danilo Caita Tapia****, S Rodriguez Arevalo, E Borja Goyeneche, J Olaya Florez, B Gamboa Mendoza,* Universidad Nacional de Colombia, Colombia

In this work it was studied the influence of the variation on weight percentage of Ag in TiAlSiN coating deposited on TiAlV substrate with co-sputtering technique. The structural analysis was performed by X-ray diffraction (XRD) and chemical composition was performed using Energy-dispersive X-ray spectroscopy (EDS). It was evaluated the corrosion response at one hour of Electrochemical Impedance Spectroscopy (EIS) performed on samples in different solutions that simulate physiological fluids such as 3.5%NaCl at human body temperature (aprox. 38°C), physiological serum and ringer lactate. Those results were compared with an EIS corrosion test in 3.5%NaCl solution at an ambient temperature. It is shown that there is a peak in silver content for which is reached the best corrosion resistance performance, wich in addition to the antibacterial capacities of Ag, makes this coating an optimal candidate for biomedical applications.

10:00am **B4-1-TuM-7 Adhesion Strength of Titanium Carbide Thin Film Coatings on Surface Microstructure Controlled WC-Co**, ***Takeyasu Saito****, C Tanaka, N Okamoto,* Osaka Prefecture University, Japan*; A Kitajima, K Higuchi,* Osaka University, Japan

Chemical vapor deposited (CVD) or physical vapor deposited (PVD) hard material coating technique on the cemented-tungsten carbide (WC-Co) is widely used for molds and cutting tools, which plays an important role in a lot of manufacturing industry. Plasma enhanced chemical vapor deposition (PECVD) and PVD have some merits like lower deposition temperature (< 500°C) than thermal CVD and high through-put, however, the films usually have low adhesion strength. Then, life of molds and cutting tools obtained PVD are usually shorter than that with CVD.

In this study, several surface pretreatment methods were investigated to increase surface roughness to enhance adhesion strength. The procedure include, dry etching by CF_4 plasma discharge for 15 to 120 min in the temperature change from R.T. to 500°C. Chemical treatment with aqua regia (3HCl:HNO_3) for 3 min at 25 to 60°C. After pretreatment, TiC coatings were formed by sputtering with TiC target or PECVD with $TiCl_4$ and CH_4. Surface roughness, deposition rate, composition ratio and chemical bond, hardness and adhesion strength of WC-Co and TiC coating film ewre evaluated AFM, surface profiler, XPS, dynamic ultra-micro hardness tester, and scratch tester, respectively.

Figure 1 shows the relationship between the surface roughness (Ra) and critical load of sputtered TiC hard coating layer on surface treated WC-CO. With the CF_4 plasma treatment, the maximum load of 12.1 N with Ra = 46 nm. However, with the aqua regia treatment, the maximum load of ca. 70 N more than Ra = 80 nm. There are still scatters less than Ra = 80 nm. The cause of delamination was thought to be the detailed substrate morphology or chemical states after etching and poor step coverage of sputtered TiC coating layer. Figure 2 shows the relationship between the surface roughness (Ra) and critical load of PECVD TiC hard coating layer on surface treated WC-CO with aqua regia. Compared with fig. 2(right), the critical load is worse. We are still investigating the reason but are considering that the quality PECVD TiC film is poor at this moment

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-2-TuA

Properties and Characterization of Hard Coatings and Surfaces II

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

1:40pm **B4-2-TuA-1 Fracture Toughness Enhancement in Superlattice Hard Coatings***, **Rainer Hahn**[1], M Bartosik, H Riedl,* TU Wien, Institute of Materials Science, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

Physical vapour deposited (PVD) ceramic hard coatings are widely used in industrial applications as protective, wear reducing coatings. Their combination of good mechanical properties such as high hardness, a low friction coefficient, and their chemical resistance enable the application in harsh environments. However, a strong limitation is the relatively low fracture tolerance (brittle behaviour), depicting especially in cutting applications a major challenge.

In this contribution, we show experimental results of *in-situ* microcantilever bending tests on nanolayered TiN–CrN coatings, referred to as superlattices, overcoming this unfavourable behaviour. We found a maximum in fracture toughness (K_{IC}) at bilayer periods of ~6 nm [1], similar to the well-known peak for the indentation hardness reported by Helmersson et al. [2]. For both, K_{IC} and the hardness, we observe an increase by ~50 % compared to the rule of mixture of the constituents. The beneficial effect of a careful structural design on the fracture toughness will be shown for reactive magnetron sputtered as well as arc evaporated superlattice coatings. Importantly, the coatings synthesized in the industrial scale arc evaporation plant (Oerlikon Balzers Innova) show an even more pronounced superlattice effect and thus unite high hardness with reasonable toughness.

While mechanisms based on dislocation activity explain the increase in hardness, the linear elastic behaviour during our micromechanical tests suggests a different mechanism responsible. To describe this, we conducted density functional theory (DFT) calculations as well as finite element studies.

Complementary, we studied the microstructure of our coatings by X-ray diffraction experiments, scanning electron microscopy and high-resolution transmission electron microscopy. The thermal stability of our films was investigated by annealing in vacuum and ensuing experiments (XRD, hardness and fracture toughness) [3] along with differential scanning calorimetry (DSC) investigations.

[1] R. Hahn, M. Bartosik, R. Soler, C. Kirchlechner, G. Dehm, P.H. Mayrhofer, Superlattice effect for enhanced fracture toughness of hard coatings, Scripta Mat. 124 (2016) 67.

[2] U. Helmersson, S. Todorova, S.A. Barnett, J.-E. Sundgren, L.C. Markert, J.E. Greene, Growth of single-crystal TiN/VN strained-layer superlattices with extremely high mechanical hardness, J. Appl. Phys. 62 (1987) 481.

[3] R. Hahn, M. Bartosik, M. Arndt, P. Polcik, P.H. Mayrhofer, Annealing effect on the fracture toughness of CrN/TiN superlattices, Int. J. Refract. Met. H. 71 (2018) 352-356.

2:00pm **B4-2-TuA-2 Simultaneous Topographical and Electrochemical Mapping using Scanning Ion Conductance Microscopy - Scanning Electrochemical Microscopy (SICM-SECM)***, W Shi, G Mendoza,* ***Byong Kim****, K Lee,* Park Systems Corporation, USA

Lately, scanning ion conductance microscopy (SICM), has emerged as a versatile non-contact imaging tool. To obtain spatially-resolved electrochemical information, scanning electrochemical microscopy (SECM), also known as the chemical microscope, has been developed. Hybrid SICM-SECM techniques have been developed, in which the SICM compartment provides the accurate probe-sample distance control, while the SECM compartment measures the faradaic current for electrochemical information collection.

In this work, we demonstrate the use of an Atomic Force Microscopy (Park NX10) in combination with an ammeter for concurrent topography imaging and electrochemical mapping. The SICM-SECM probe consisted of a Au crescent electrode (AuE) on the peripheral of a nanopipette. High resolution probe-substrate distance control was obtained by the ion current feedback from SICM, while simultaneous electrochemical signal collection was achieved via the AuE from SECM. As a proof-of-concept experiment, a Au/Pyrex pattern standard sample was imaged with the SICM-SECM technique. The Au bar and the Pyrex substrate were clearly resolved from the SICM topography image, with the bar height and pitch width closely matching the actual values. In terms of the electrochemical property mapping, higher Faradaic current was seen when the probe was scanned over Au bar as a result of redox cycling, while lower Faradaic current was observed when the probe was over Pyrex substrate due to hindered diffusion. The capability of the SICM-SECM technique described here holds promise of many exciting applications in the field of electrochemistry, battery research and metallurgical coatings.

4:00pm **B4-2-TuA-8 Performance Comparison of Two Diffusion Models for Describing the Growth Kinetics of Iron Boride Layers***, M Ortiz-Domínguez,* Universidad Autónoma del Estado de Hidalgo, México*; O Gómez-Vargas,* ***José Solis-Romero****,* Instituto Tecnológico de Tlalnepantla, México*; G Ares de Parga,* Instituto Politécnico Nacional, México*; J Oseguera-Peña,* Tecnológico de Monterrey, México

In selecting and designing materials for certain engineering applications is an important factor. Likewise, one of the most important reasons for the machinery parts to suffer damage and fail is wear. The boriding process is adequate to increase the surface hardness and a very significant resistance against some acids, bases, metal solutions and high temperature oxidizing are among the advantages of boriding over other surface hardening methods to extend its lifetime. An indispensable tool to choose the suitable process parameters for obtaining boride layer of an adequate thickness is the modeling of the boriding kinetics. Moreover, the simulation of the growth kinetics of boride layers has gained great interest in the recent years. In this study, the AISI O1 steel was pack-borided in the temperature range of 1123-1273 K for different treatment times ranging from 2 to 8 h. Two kinetic models were proposed for estimating the boron diffusion coefficients through the Fe_2B layers. Displacements of the interface (Fe_2B/substrate) resulted from a difference of the arrival flux of the interstitial boron atoms to one phase. The mass balance equations were formulated. The measurements of the thickness (Fe_2B), for different temperature of boriding, were used for calculations. As a result, the boron activation energy for the AISI O1 steel was estimated as 197.20 kJ mol^{-1}. This value of energy was compared between both models and with other literature data. In addition, to extend the validity of the present models, two additional boriding conditions were done. The Fe_2B layers grown on AISI O1 steel were characterized by use of the following experimental techniques: X-Ray Diffraction (XRD), Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS) .

4:20pm **B4-2-TuA-9 Microstructure and Surface Strength of Chemically Modified WC-Co for Adhesive Strength Improvement***,* ***Daichi Kiyokawa****, C Tanaka, T Saito, N Okamoto,* Osaka Prefecture University, Japan*; A Kitajima, K Higuchi,* Osaka University, Japan

Chemical vapor deposited (CVD) or physical vapor deposited (PVD) hard material carting technique is widely used the cemented-tungsten carbide (WC-Co) for molds and cutting tools, which plays an important role in a lot of manufacturing industry. However, the adhesive strength is one of the issues for reliable mold preparation.

In this study, substrate is pretreated by chemical treatment with aqua regia ($3HCl:HNO_3$) for 1 to 5 min at 25 to 60°C to remove Co from the WC-Co surface and to increase surface roughness to enhance adhesion strength. The hardness of films was measured by dynamic ultra-micro hardness tester (Shimadzu Co. DUH-211). Pretreated WC-Co substrates are measured for bulk strength with 200 gf of test load as well as for surface strength with 25 gf of test load.

Figure 1 shows Martens hardness (HM) of WC-Co bulk after pretreatment. Hardness of pretreated substrate became gradually lower. Figure 2 shows HM of WC-Co surface after pretreatment. Hardness of pretreated substrate became lower, even after 1min/25°C treatment. In addition, the difference in HM increased with higher temperature an longer treatment period. The brittleness of WC-Co surface after surface treatment should be eliminated. The TiC-based hard coating deposition of surface treated WC-Co will be discussed.

[1] **Student Award Nominee**

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B7-TuA

Plasma Diagnostics and Growth Processes

Moderators: Arutiun P. Ehiasarian, Sheffield Hallam University, **Yolanda Aranda Gonzalvo**, Consultant, USA

1:40pm **B7-TuA-1 On the Growth of TiO_x Coatings by Reactive Magnetron Sputtering from Metallic and Ceramic ($TiO_{1.8}$) Targets: A Joint Modelling and Experimental Story**, ***Romain Tonneau***, *P Moskovkin,* University of Namur, Belgium*; W De Bosscher,* Soleras Advanced Energy, Belgium*; A Pflug,* Fraunhofer Institute for Surface Engineering and Thin Films, Germany*; S Lucas,* University of Namur, Belgium

This work reports the study of the growth mechanisms involved in TiO_x thin film deposition by magnetron sputtering. An Ar-O_2 plasma chemistry obtained by dual magnetron setup operating in DC mode is used. Growth from both metallic and $TiO_{1.8}$ targets are compared. Isotopic $^{18}O_2$ is used as reactive gas for all different configurations. The aim is to differentiate oxygen coming from ceramic targets and oxygen coming from the gas phase. Indeed, using ion beam analysis techniques such as Rutherford Backscattering Spectroscopy it is possible to precisely analyze Ti, ^{16}O and ^{18}O content of the samples. Other investigation techniques such as AFM, SEM … are also used to fully characterize deposited coatings. In order to study the effect of energetic ions bombardment of samples during deposition, 70° and normal incidence samples are compared. In addition to sample's characterization, Langmuir probe and energy flux probe are used to obtain plasma phase properties.

In a second part, simulations tools are used to predict both discharge and coating's properties. In order to simulate the complete plasma process, three different software are used. Each one is handling a defined step of the process (i) neutral particle motion, (ii) charged particle motion and (iii) film growth. We will discuss the comparison between simulation predictions and experimental investigations. Those two approaches allow us to achieve a better understanding on the growth of oxide layers by reactive magnetron sputtering and how plasma parameters influence coating properties.

2:00pm **B7-TuA-2 Titanium Atom and Ion Number Density Evolution in Reactive HiPIMS with Oxygen, Nitrogen and Acetylene Gas**, *M Fekete,* Masaryk University, Brno, Czech Republic*; D Lundin,* Université Paris-Sud/CNRS, France*; K Bernatova, P Klein, J Hnilica,* ***Petr Vasina****,* Masaryk University, Brno, Czech Republic

Reactive high power impulse magnetron sputtering (R-HiPIMS) offers a great opportunity for high quality coating production thus understanding the processes accompanying deposition is of great importance. The hysteresis curve in R-HiPIMS generally exhibits a narrower shape compared to dcMS, or it can even be entirely suppressed, which is beneficial for high-rate deposition of stoichiometric compound films. The main reason of the hysteresis suppression is not yet completely understood. A recently developed effective branching fraction method is utilized to determine absolute ground state number densities of sputtered titanium species from the optical-emission signal. We report on evolutions of titanium atom and ion ground state densities in R-HiPIMS discharges in oxygen, nitrogen and acetylene gases for constant mean power and pulse duration, when varying the repetition frequency. A fast feedback system is employed to allow working in the transition region of the hysteresis curve in a well-controlled manner. The ionization fraction of sputtered species increases with the partial pressure of the reactive gas. The increased ionization of titanium is attributed to the combination of the following effects: a longer residual time of sputtered species in the target vicinity; a higher maximal discharge current attained at the end of the pulse; lower amount of sputtered species due to the target poisoning which may positively affect electron distribution function. It is furthermore found that the hysteresis curve shape changes when varying the repetition frequency at the same mean power. The difference is more pronounced for R-HiPIMS with higher sputtered species ionization fraction. The experimental results are compared to the results obtained by a reactive ionization region model (R-IRM). The absolute ground state number densities of Ti atoms and Ti ions measured at the target vicinity are also substituted into the Berg model modified to include ion back attraction, and a rather good match between the measurements and simulation results for different experimental conditions is found.

2:20pm **B7-TuA-3 Phase Formation during Sputtering of Copper in Argon/Oxygen Mixtures**, *D Altangerel,* ***Diederik Depla****,* Ghent University, Belgium

Structure zone models give an overview of the microstructure as a function of the deposition conditions. It has been shown by our research team that these overviews can be interpreted in a quantitative way by studying the ratio between the diffusivity (D) and the deposition flux (F)[1-3]. The deposition flux can easily be derived from the deposition rate. To calculate the diffusivity the available energy per deposited atom (EPA) needs to be quantified which becomes possible by measuring the total energy flux with a passive calorimetric probe. In this paper, this approach is applied to understand the phase formation during reactive sputtering of copper in an argon/mixture. The influence of the total pressure, and the discharge current was investigated. Within the experimental range hardly any changes in the EPA could be noticed, illustrating that the phase formation in the case of copper oxide thin films is solely defined by the oxygen partial pressure in the system. In the case of pure tenorite (CuO) thin films deposited at relative high oxygen partial pressures, the EPA could by increased, and it is shown that this leads to less crystalline films. The origin of this behavior is further investigated by energy-resolved mass spectrometry.

[1] Review paper : S. Mahieu, D. Depla, Journal of Physics D: Applied Physics 42 (2009) 053002

[2] Critical review paper : D. Depla, B. Braeckman, Thin Solid Films, (2016) 90-93

[3] J. Xia, W. Liang, Q. Miao, D. Depla, Applied Surface Science 439 (2018) 545–551

2:40pm **B7-TuA-4 Plasma Diagnostics During Growth of Transparent Conductive Oxide Thin Films by Magnetron Sputtering**, ***Eugen Stamate****,* Technical University of Denmark, Denmark **INVITED**

Transparent and conductive materials are important for a large number of applications including: touch screens, solar cells, smart windows and light emitting diodes. Oxides doped with metals, generically known as transparent conductive oxides (TCO) are successfully used nowadays, with indium tin oxide (ITO) as the best material. However, the high demand for large area applications, conflicts with the reduced abundance of indium. This motivation sustains an intensive research on alternative materials with aluminum doped zinc oxide (AZO) as one of the most promising choices. There are several methods used to deposit AZO. Among them, magnetron plasma sputtering is successfully used for ITO on large area substrates and it is also investigated as a viable cost effective method for AZO. However, the resistivity of AZO thin films is about 5 to 10 time higher than ITO, with promising values only for limited areas on the substrate. One of the main reasons is the electronegativity of oxygen that forms negative ions, resulting in a growth mechanism assisted by energetic ions with a spatial distribution correlated with the erosions tracks. In this context, a proper deposition process requires spatially-resolved plasma diagnostics in direct correlation with spatially-resolved thin film properties. This work reviews the status in plasma diagnostics during TCO growth with special emphasis on AZO. New results by mass spectrometry, optical emission and probes are also presented, both for disk and rotatable cathodes operated in DC, RF and MF using oxide (ZnO/Al_2O_3, 2, 2.5 and 3% Al) and metallic targets (Zn, 2 and 3% Al). Pressure, target to substrate distance and discharge power have been investigated as discharge parameters with the aim of obtaining a resistivity below 10^{-3} W cm over the whole length of the sample (50 mm for disk cathode and 200 mm for rotatable cathode). The resistivity, transmittance and film thickness were measured with a spatial resolution of 2 mm. XPS, XRD, TOF-SIMS and SEM were used for surface characterization. It is shown that the AZO resistivity can change with two orders of magnitude over 10 mm span on the substrate, a behavior that can be correlated with plasma parameters and the growth mechanism.

4:20pm **B7-TuA-9 On Three Different Ways to Quantify the Degree of Ionization in Sputtering Magnetrons**, *A Butler,* Université Paris-Sud, Université Paris-Saclay, France*; N Brenning,* Université Paris-Sud, Université Paris-Saclay, Sweden*; M Raadu,* KTH Royal Institute of Technology, Sweden*; J Gudmundsson,* University of Iceland, Iceland*;* ***Tiberiu Minea****, D Lundin,* Université Paris-Sud, Université Paris-Saclay, France

Quantification and control of the fraction of ionization of the sputtered species are crucial in magnetron sputtering, and in particular in high-power impulse magnetron sputtering (HiPIMS), yet proper definitions of the various concepts of ionization are still lacking. In this contribution, we distinguish between three approaches to describe the degree (or fraction) of ionization: the ionized flux fraction F_{flux}, the ionized density fraction

$F_{density}$, and the fraction α of the sputtered metal atoms that become ionized in the plasma (sometimes referred to as probability of ionization). By studying a reference HiPIMS discharge with a Ti target, we show how to extract absolute values of these three parameters and how they vary with peak discharge current. Using a simple model, we also identify the physical mechanisms that determine F_{flux}, $F_{density}$, and α, as well as how these three concepts of ionization are related. This analysis finally explains why a high ionization probability does not necessarily lead to an equally high ionized flux fraction or ionized density fraction.

5:00pm **B7-TuA-11 Characterization of Microwave Surfatron Plasma-enhanced-ALD System for Low-temperature Deposition of Thin Oxide Films***, **Martin Cada**, D Tvarog,* Institute of Physics CAS, v. v. i., Czech Republic*; J Kim,* ISAC Research Inc., Republic of Korea*; A Poruba,* SVCS Process Innovation s.r.o., Czech Republic*; Z Hubicka,* Institute of Physics CAS, v. v. i., Czech Republic

The preparation of ultra-thin film is crucial for the development of cutting-edge technologies in the field of microelectronics, optoelectronics, nanotechnology or catalysts. Furthermore, covering 3-D objects in a nanometer scale requires a high degree of uniformity of deposited thin films preserving high aspect ratio of complex shape objects. Atomic layer deposition (ALD) has proven to be almost an indispensable deposition technique for conformal deposition of mostly metal or oxide thin films. Plasma-enhanced ALD (PE-ALD) process brings energy for surface reactions between precursors and reactants through electrons, ions, radicals or excited particles. Many studies have shown that the PE-ALD process is able to operate at significantly lower substrate temperatures. In this work, a microwave surfatron plasma source as alternative to CCP, ICP or other remote plasma sources was used for activation of reactants during the PE-ALD process. We carried out measurements with the Langmuir probe to obtain spatial map of electron temperature, plasma density and potentials in the ALD chamber designed for deposition on wafers with diameter 100 mm during typical deposition conditions of TiO_2, Al_2O_3 and TiN thin films. The plasma parameters were investigated for different working gas pressures and mixtures. Obtained results proved that radial homogeneity of the plasma density could be improved if mass flow rate of working gas is reduced. On the other hand, for higher pressure of the working gas the plasma density rapidly decreased in axial distance from the surfatron nozzle outlet. Results clearly demonstrated that spatial inhomogeneity of the plasma parameters correlates with thin film properties. The possibilities of deployment of the multi-nozzle surfatron system for achieving a sufficient level of homogenization of the plasma parameters was suggested. Effect of substrate temperature and microwave power delivered into the surfatron on deposited thin film properties was studied too. The Raman spectroscopy proved that substrate temperature above 200°C led to anatase phase formation of TiO_2 thin films whilst lower temperatures produced amorphous thin films. Further, gradually increased microwave power resulted in the rise of thin film thickness measured by the spectroscopic ellipsometry for constant number of ALD cycles. Impact of the microwave power on the Growth per Cycle (GPC) parameter was studied by the optical emission spectroscopy detecting evolution of oxygen or nitrogen atoms and radicals.

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Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-3-WeM

Properties and Characterization of Hard Coatings and Surfaces III

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

8:20am **B4-3-WeM-2 Physical Properties of Nano-structured Chromium Nitride Hard Coatings obtained by RF Physical Vapor Dynamic Glancing Angle Deposition**, *M Jimenez, V Antunes, S Cucatti, A Riul, L Zagonel,* UNICAMP, Brazil*; C Figueroa,* Universidade de Caxias do Sul, Brazil*; D Wisnivesky,* UNICAMP, Brazil*; **Fernando Alvarez,*** Instituto de Física, UNICAMP, Brazil

Nanostructures CrN films are obtained by combining *RF Physical Vapor Dynamic Glancing Angle Deposition* (PV-DGAD) and Logic Programmable Computer (PLC) controlled substrate motion. By appropriated substrate oscillation frequency, the physical properties such as the micro-nanostructure, morphology, hardness, texture, crystallite size are feasible to be tailored. Samples are deposited by moving the substrate forward (-ϕ=> +ϕ) a back (+ϕ => -ϕ) by controlling the angular velocity ω=dϕ/dt. The angle ϕ is measured perpendicular to the substrate (ϕ=0, Cr target parallel to the substrate). We report the physical properties of samples obtained by moving the substrate with ω(t) constant and square shape functions. The time dependence angle of the precursors atoms impinging the substrate prompts the formation of wavy-like and zigzag periodic nano-crystalline columnar nano-structures with interesting physical properties. The physical characteristics of the CrN coating such as morphology, residual stress, nano-hardness, crystallite size and texture of the columnar multi-structured films are customized by the PLC motion of the substrate. Also, X-ray spectra show that the oscillation of the substrate allows the appearance of a periodic crystalline orientations that strongly depends on ω(t). Finally, these properties of the deposition technique open the possibility to control the (un)isotropy of the hard coatings for specific applications.

Keywords: Hard Coating, Chromium nitride, Dynamic Glancing angle deposition

8:40am **B4-3-WeM-3 Synthesis and Characterization of Sputter Deposited Hard Coatings within the Quasibinary System TiB_2–VB_2**, ***Christian Mitterer,*** *V Terziyska, M Tkadletz, L Hatzenbichler, D Holec,* Montanuniversität Leoben, Austria*; V Moraes,* Institute of Materials Science and Technology, TU Wien, Austria*; A Lümkemann,* PLATIT AG Advanced Coating Systems, Switzerland*; M Morstein,* Hightech Zentrum Aargau AG, Switzerland*; P Polcik,* Plansee Composite Materials GmbH, Germany

TiB_2 coatings on cutting tools have become state-of-the-art in high-performance machining of nonferrous alloys, due to their superior hardness, thermal stability and low adhesion tendency to workpiece material. These properties stem from strong covalent B-B bonds within the hexagonal TiB_2 lattice, which consequently results in high brittleness limiting their application. Thus, in this work, coatings within the quasibinary system TiB_2–VB_2 have been investigated, with the goal to tune their chemical bonds to overcome these limitations. Coatings with thicknesses of 2 ± 0.5 µm have been synthesized by d.c. magnetron sputter deposition from powder metallurgically produced $(Ti,V)B_2$ composite targets with 2-inch-diameter and VB_2 fractions of 0, 7, 13, 25, and 100 mol%. All coatings are characterized by a strongly (001) oriented hexagonal AlB_2-type $(Ti,V)B_2$ solid solution phase with a Vegards-like gradual shift of X-ray diffraction peaks from TiB_2 to VB_2. While the compressive stress within the TiB_2 coatings reaches a maximum of -1.4 GPa, VB_2 addition results in stress relaxation to about -0.3 GPa, independent of the VB_2 content. Despite this low stress of $(Ti,V)B_2$ coatings, their hardness and elastic modulus is largely unaffected by the VB_2 addition, reaching values of about 45 GPa and 420 GPa, respectively. In addition, $(Ti,V)B_2$ coatings sputter deposited from targets with 25 mol% VB_2 show superior friction and wear properties during ball-on-disk testing against Al_2O_3 at room temperature and at 400°C, outperforming pure TiB_2 coatings. Finally, the results obtained are corroborated by ab-initio calculations of elastic properties within the TiB_2–VB_2 quasibinary system.

9:00am **B4-3-WeM-4 Deposition-controlled Stabilization of Metastable fcc-(Al,Ti)N in CVD and PVD Coatings**, ***Ulrike Ratayski,*** Technische Universität Bergakademie Freiberg, Germany*; M Höhn,* Fraunhofer IKTS, Germany*; B Scheffel,* Fraunhofer FEP, Germany*; F Fietzke,* Fraunhofer Institute for Organic Electronics, Electron Beam and Plasma Technology FEP, Germany*; M Motylenko, D Rafaja,* Technische Universität Bergakademie Freiberg, Germany

The addition of aluminum nitride to titanium nitride is known to improve the high-temperature oxidation resistance of TiN-based coatings. Furthermore, low or medium concentrations of Al increase also the hardness of the (Ti,Al)N coatings [1]. High Al contents lead typically to an enhanced decomposition of titanium aluminum nitride into Ti-rich (Ti,Al)N with the face centered cubic (fcc) structure and wurtzitic AlN, and to the degradation of the mechanical properties of the Al-rich (Al,Ti)N coatings. In order to be able to achieve good high-temperature oxidation resistance and high hardness concurrently, metastable Al-rich fcc-(Al,Ti)N must be stabilized.

In this comparative study, the mechanisms stabilizing metastable Al-rich fcc-(Al,Ti)N are discussed and tested on the Al-rich (Al,Ti)N coatings containing more than 50 mol % AlN, which were deposited using chemical vapor deposition (CVD), spotless arc evaporation (SAD) and pulsed magnetron sputtering (PMS). The mechanisms stabilizing the thermodynamically metastable phases were concluded from the microstructure analyses that were performed using X-ray diffraction, transmission electron microscopy with high resolution, X-ray spectroscopy (EDX) and electron-energy loss spectroscopy (EELS).

In the (Al,Ti)N coatings prepared by CVD, three-phase composites consisting of fcc-(Ti,Al)N, fcc-(Al,Ti)N and w-AlN have formed. Although w-AlN is known to deteriorate the mechanical properties of the (Al,Ti)N coatings, the interaction of these phases retarded the decline of the hardness up to x_{AlN} ~ 0.9. In the (Al,Ti)N coatings deposited by PMS, the formation of w-AlN was avoided up to x_{AlN} ~ 0.65. The Al-rich fcc-(Al,Ti)N phase was apparently stabilized by fluctuations of the Al (and Ti) concentration. The concentration of Al (and Ti) showed almost bimodal distribution in these coatings. In the (Al,Ti)N coatings deposited using SAD, the Al-rich fcc-(Al,Ti)N was stabilized mainly by a low ad-atom mobility, which promoted the formation of supersaturated fcc-(Al,Ti)N.

[1]D. Rafaja, C. Wüstefeld, M. Dopita, V. Klemm, D. Heger, G. Schreiber, M. Šíma, Surf. Coat. Technol. 203 (2008) 572-578]

Keywords: metastable fcc-(Al,Ti)N, microstructure, chemical vapor deposition, spotless arc evaporation, pulsed magnetron sputtering, XRD, TEM

9:20am **B4-3-WeM-5 Oxidation Resistance of AIP Deposited AlCrN and AlTiN Coatings with High Al Compositions**, ***Kenji Yamamoto,*** *H Nii,* Kobe Steel, Ltd., Japan

Al containing transition metal nitrides undergo a characteristic phase transition from cubic B1 to hexagonal B4 structure as the Al content is increased. This change in crystal structure is known to affect not only mechanical property, but also chemical property such as oxidation resistance [1]. AlCrN and AlTiN are one of compounds among such system and applied tribological components such as cutting tool, die and molds for superior mechanical and oxidation resistance at elevated temperatures. A series of AlCrN and AlTiN coating with different Al contents were deposited by cathodic arc ion plating with different substrate bias voltage. Crystal structure of the coatings were examined by XRD and oxidation behavior was investigated by annealing samples in air at 800, 900 and 1000 °C for 30min and surface O composition was measured by EDX and AES for O depth profiling.

Both AlCrN and AlTiN coating showed change in crystal structure depending on the substrate bias, especially Al content is more than 70 at% for AlCrN and 50 at% for AlTiN. These coatings contain hexagonal phase in the coating at low substrate biases and became cubic single phase as the substrate bias is increased. In case of AlCrN, the oxidation behavior seems influenced by the crystal structure and much better oxidation resistance was observed for cubic single phase coating independent of Al content. In case of AlTiN, however, such crystal structure dependent oxidation behavior was not observed. X-ray diffraction analysis of these AlCrN and AlTiN coatings suggests systematic change in grain size corresponding to the change in substrate bias as indicated by width of the diffraction peak. From this observation, it can be concluded that change in oxidation resistance is more likely correlating to the change in grain size of the coating rather than crystal structure.

References:

[1] Reiter et al. Surf. Coat. Technol., Vol. 200, (2005) 2114

9:40am **B4-3-WeM-6 Standing Contact Fatigue Behavior of Nitrided AISI 316L Steels***, **Daybelis Fernández-Valdés**, A Meneses-Amador, G Rodríguez-Castro, I Campos-Silva,* Instituto Politecnico Nacional Grupo Ingeniería de Superficies, México*; A Mouftiez,* ICAM Lille, Matériaux, France*; J Nava-Sánchez,* Tecnologico de Estudios Superiores de Chalco, México

In this work an experimental-numerical evaluation of the standing contact fatigue testing of a nitrided AISI 316L steel is developed. The nitride layers were formed at the surface of a AISI 316L steel by salt bath nitriding process at a temperature of 580 ° C for 1, 3 and 5 hours of exposure time, obtaining three different layer thicknesses. In order to know the mechanical response and the different mechanisms of damage associated with the standing contact fatigue test, Hertzian tests were performed on a MTS machine by cyclic loading of a sphere on a flat surface formed by the layer / substrate system. The standing contact fatigue test was developed through two main stages. Firstly, the critical loads for each treatment condition were determined by monotonic tests, where the appearance of circular cracks were considered as a failure criterion. Subsequently, cyclic subcritical loads were applied at a frequency of 5 Hz. A numerical model based on the finite element method was developed to evaluate the stress field generated in the mechanical contact. The results indicate that the thinner coating exhibits better resistance to standing contact fatigue.

11:00am **B4-3-WeM-10 Effect of Composition on Toughening Mechanism of $V_{1-x}Mo_xN$ Nanocrystalline Thin Film***, **Yi-Qun Feng**, J Huang,* National Tsing Hua University, Taiwan

The purpose of this study were to investigate the toughening mechanism of $V_{1-x}Mo_xN$ nanocrystalline thin film with different composition of Mo, and compare the texture, residual stress and fracture toughness with each specimen. It is commonly acknowledged that nanocrystalline ceramics with high strength and hardness, while always show low ductility, which limits their applications. Recently, Sangiovanni et al. [1] predicted the $V_{0.5}Mo_{0.5}N$ coating with high hardness and ductility by ab initio density functional theory (DFT), and it has been verified by experiments that $V_{0.5}Mo_{0.5}N$ is more ductile than VN. However, there is lack of studies on the accurate stress and fracture toughness measurements of $V_{1-x}Mo_xN$ and the associated fracture mechanisms. Also it is important to understand the toughness enhancing mechanisms compared with different compositions of $V_{1-x}Mo_xN$. Therefore, this study aimed to investigate the relationship of texture, residual stress and toughness of the different compositions of $V_{1-x}Mo_xN$. $V_{1-x}Mo_xN$ thin films about 1000 nm were deposited on Si substrate by unbalanced magnetron sputtering (UBMS), the compositions of Mo were set to 0.1, 0.2, 0.3, 0.4 and 0.5 by adjusting Mo target currents. After deposition, the ratio of V/Mo and (V+Mo)/N were determined by X-ray photoelectron spectroscopy (XPS), the thickness of all specimens were confirmed by auger electron spectroscopy (AES) and scanning electron microscope (SEM). X-ray diffraction (XRD) was used to characterize the structure and the texture. Besides, the residual stress of the specimens was measured by laser curvature method (LCM) and average X-ray strain (AXS) combined with elastic constant from nanoindentation [2], the hardness was assessed by nanoindentation, and the internal energy induced cracking (IEIC) method was used to evaluate the fracture toughness.

[1] D. G. Sangiovanni, V. Chirita, L. Hultman, Phys. Rev. B, 81 (2010) 104107.

[2] A.-N. Wang, C.-P Chuang, G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 262 (2015) 40.

11:20am **B4-3-WeM-11 Influence of Mo Contents on Elevated Temperature Tribological Characteristics of CrAlMoSiN Nanocomposite Coating***, **Yu-Chia Lin**, H Tao, J Duh,* National Tsing Hua University, Taiwan*; J Lee,* Ming Chi University of Technology, Taiwan

CrAlMoSiN nanocomposite coatings were produced by doping Mo into the CrAlSiN nanocomposite matrix via radio frequency magnetron sputtering. CrAlMoSiN thin films with different Mo contents were deposited on both Si-wafer and Inconel-718 substrate by controlling the Mo target working power. Since CrAlSiN nanocomposite coatings exhibit superior high temperature wear resistance, the addition of Mo into CrAlSiN nitride coatings will offer extra self-lubricating characteristic, which leads to lower friction coefficient. By doping Mo in to CrAlSiN coating via composition control, CrAlMoSiN coatings with high temperature wear resistance and reduced friction coefficient could be developed.

The chemical compositions of as-deposited coatings were identified by a FE-EPMA. The tribological property was evaluated by a tribometer with temperature control unit. The wear tracks were analyzed by an Alpha-step to calculate the wear rate. The nano-hardness (HIT) and reduced elastic modulus (EIT*) were examined by a nano-indenter. Further, microstructure of wear tracks was analyzed by FE-SEM and HR-TEM. The phase transformations were observed by a Gazing Incidence XRD and XPS.

11:40am **B4-3-WeM-12 Characterization of Cosputtered W –Si– N Coatings***, **Yu-Heng Liu**,* National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan*; B Liu, Y Chen,* National Taiwan Ocean University, Taiwan

Monolithic and multilayered W–N and W–Si–N coatings were fabricated through direct current magnetron cosputtering with a nitrogen flow ratio (N_2/(N_2 + Ar)) of 0.4 at substrate holder rotation speeds of 0 and 5 rpm, respectively. The characteristics and oxidation behaviors of the W–N and W–Si–N coatings were investigated by nanoindentation technique, X-ray diffraction, X-ray photoelectron spectroscopy, and transmission electron microscopy. The mechanical properties of crystalline W–N coatings correlated to their texture and residual stress. The monolithic $W_{77}N_{23}$ samples located nearest to the W target exhibited a high deposition rate of 18.0 nm/min, a strong (200) texture coefficient, a high nanoindentation hardness of 32.7 GPa, a high Young's modulus of 392 GPa and a residual stress of −3.2 GPa. The addition of Si into the W–N matrix transformed the coatings to be an X-ray amorphous phase dominated structure comprising constitutions of Si_3N_4, W_2N, and W. The preferential formation of Si_3N_4 declined the residual stress and mechanical properties of the W–Si–N coatings with increasing the Si contents. By contrast, the oxidation resistance was improved by adding a Si content > 24 at.% after annealing at 600 ◦C in a 1% O_2–99% Ar atmosphere.

12:00pm **B4-3-WeM-13 RF Input Power Effect on Microstructure and Mechanical Properties of TaSiN Coatings***, **Zheng-Xin Lin**, Y Liu, S Wang,* National United University, Taiwan*; M Guillon,* Polytech Lyon, France*; F Wu,* National United University, Taiwan

The TaSiN nanocomposite thin films were fabricated by a reactive radio frequency ,r.f., magnetron sputtering system with pure Ta and Si sources. The Ar/N_2 flow ratio was fixed at 18/2 sccm/sccm, while r.f. input powers for Ta and Si were from 50 to 200W and from 50 to 150W, respectively. The Si contents doped in the coating ranged from 0 to approximately 25 at.%. The plasma of various process conditions were investigated by Optical Emission Spectroscopy.Characterizations by XRD, TEM, SEM revealed the dependence of Si dopeing and SiN_x phases on the preferred orientation, crystalline behavior, microstructure. Mechanical properties through wear tester, Rockwell.C and nano-indentation were evaluated to check the durability, adhesion and hardness, respectively. When the content of silicon reaches 17 at.%, the TaSiN structure evolved from crystallization to amorphous, leading to a significant degradation of mechanical properties. The TaSiN with lower Si contents exhibited TaN with SiN_x phase and processed superior mechanical strength.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B4-4-WeA

Properties and Characterization of Hard Coatings and Surfaces IV

Moderators: Naureen Ghafoor, Linköping Univ., IFM, Thin Film Physics Div., **Ulrich May**, Robert Bosch GmbH, Diesel Systems, **Fan-Bean Wu**, National United University, Taiwan

2:00pm **B4-4-WeA-1 Effect of Ti Interlayer on Stress Relief of ZrN/Ti Bilayer Thin Films on Si Substrate**, ***Jia-Hong Huang**, T Zheng,* National Tsing Hua University, Taiwan

Pure metal interlayers have been widely used to enhance adhesion and relieve residual stress in hard coatings. However, the design of interlayer thickness for stress relief was mostly empirical without quantitative basis. The objectives of this study were to investigate the effect of metal interlayer on stress relief of hard coatings, and to establish a physical model correlating plastic deformation of the interlayer with stress relief. ZrN/Ti bilayer thin films on Si substrate was chosen as the model system. ZrN/Ti specimens with different interlayer thicknesses and with ZrN coatings deposited at different bias voltages were prepared using unbalanced magnetron sputtering. Wafer curvature method and average X-ray strain combined with nanoindentation technique [1,2] were employed to accurately measure the residual stresses in the entire specimen and individual layer, respectively. Experimental results showed that the extent of stress relief, ranging from 59.7 to 80.4%, increased with interlayer thickness, while decreased with increasing stress transferring from top ZrN layer. The efficiency of stress relief decreased with increasing interlayer thickness, but varied irregularly with the stress transferring from ZrN layer. A physical model was developed to account for the stress relief due to plastic deformation of the interlayer, based on the energy balance between elastic stored energy in ZrN and plastic work of metal interlayer. The upper limit of stress relief by the interlayer was assumed to be the necking strain of the interlayer under equibiaxial stress state. The model was verified by the experimental results. Furthermore, a critical experiment was conducted and confrimed that the model could provide a conservative estimation on stress relief for practical applications. The proposed model also indicated that the stress relief was mainly due to plastic deformation of Ti interlayer. Using the model, we could quantitatively estimate the allowable stress relief with a specific interlayer thickness or the required interlayer thickness to relieve certain amount of stress.

[1] A.-N. Wang,C.-P. Chuang,G.-P. Yu, J.-H. Huang, Surf. Coat. Technol., 262 (2015) 40.

[2] A.-N. Wang, J.-H. Huang, H.-W. Hsiao, G.-P. Yu, Haydn Chen, Surf. Coat. Technol., 280(2015) 43.

2:20pm **B4-4-WeA-2 In-situ Observation of Stress Fields during Crack Tip Shielding in Loaded Soft-hard Micro-Cantilevers using Cross-sectional X-ray Nanodiffraction**, ***Michael Meindlhumer**,* Montanuniversität Leoben, Department of Physical Metallurgy and Materials Testing, Austria*; J Todt, J Zálešák,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; S Klima, N Jäger,* Montanuniversität Leoben, Department of Physical Metallurgy and Materials Testing, Austria*; M Rosenthal, M Burghammer,* ESRF Grenoble, France*; H Hruby,* voestalpine eifeler Vacotec GmbH, Germany*; C Mitterer, R Daniel,* Montanuniversität Leoben, Department of Physical Metallurgy and Materials Testing, Austria*; J Keckes,* Montanuniversität Leoben, Austria

In recent years, cross-sectional X-ray nanodiffraction (CSnanoXRD) with a resolution down to ~30 nm has been proven to resolve depth gradients and residual stresses within individual sublayers of multi-layered thin films. In this work, the in-situ CSnanoXRD setup was used to perform micromechanical testing on a 20 µm thick film composed of four alternating hard CrN and soft Cr sublayers, each 5 µm thick, on a high-strength steel substrate. Notched freestanding and clamped cantilevers of the film thickness and a length and width of 150 and 35 µm and 200 and 40 µm, respectively, machined using focused ion beam (FIB), were tested. Multiaxial stress distributions were evaluated in stationary, stepwise loaded and unloaded cantilevers with a spatial resolution of 200 x 200 nm^2 in a cross-sectional area of ±20 µm around the FIB-fabricated notches.

While the freestanding cantilever was nearly relaxed before loading, the clamped cantilever exhibited residual stresses up to -4 GPa within the CrN sublayers and up to -500 MPa in the Cr sublayers. During the loading, high in-plane, out-plane and shear compressive stresses up to ~10 GPa were observed in CrN under the indenter and at the crack tip. In the Cr sublayers, the loading resulted in a formation of cross-sectional stress gradients and compressive-tensile-compressive stress switching at different stages of the experiments. Interestingly, it was observed in both cantilevers that the multiaxial stress concentrations at the crack tips in CrN and in Cr sublayers were blunted when approaching CrN-Cr interfaces. After the unloading, only minor changes in residual stresses in CrN were observed, compared to the stress state before loading.

In summary, the pioneering in-situ micromechanical approach coupled with X-ray nanodiffraction screening was used for the first time to determine multiaxial X-ray elastic strain/stress fields in the vicinity of notches/cracks with sub µm-resolution. The experimental data provide an understanding of the nanoscale deformation processes in nanolaminates and will be integrated into finite element simulations dealing with the evolution of crystallize size- and interface-dependent stress concentrations during elasto-plastic deformation.

2:40pm **B4-4-WeA-3 Experimentally Parameterized Simulation of an Instrumented Dry Milling Arrangement – Parameter Study Identifying Damage-relevant Coating Properties for End Mills**, ***Andreas W. Nemetz**, W Daves, T Klünsner, W Ecker,* Materials Center Leoben Forschung GmbH, Austria*; C Praetzas,* Institute of Production Management, Technology and Machine Tools (PTW), Germany*; C Czettl, J Schäfer,* CERATIZIT Austria GmbH, Austria

Solid hard metal end mills, both coated and uncoated, are used to machine difficult-to-cut materials, such as titanium alloys. Experience shows that the tool life varies greatly depending on the applied coating and the chosen process parameters. At the end of the tool life, the cutting situation is not the same as at the beginning of the process and the product quality suffers. Therefore it is of high relevance to recognize and interpret the signals, given within the process to assess its quality and estimate the remaining tool life. Especially in the field of process monitoring, temperature monitoring is a valuable addition to the prevailing force measurement. Within an instrumented milling arrangement, the measured temperature inside the coated end mill is documented. The process is numerically simulated to relate the measured core temperature in the end mill to the temperature at the cutting edge. This information is essential for the model based tool health monitoring. The synergetic use of 2D thermo-mechanical milling models and 3D thermal and mechanical models enables the prediction of the transient temperature field in milling tools. The material models describing the hard coatings and the WC-Co hard metal substrate are parameterized experimentally. The influence of hard coatings on the evolution of the evolving temperature field in end mills is investigated during dry milling. A parameter study identifies improved thermal coating material properties.

3:00pm **B4-4-WeA-4 Mechanical Properties and Cutting Performance of AlCrSiN and AlTiCrSiN Hard Coatings**, ***Liang-Chan Chao**, Y Chang,* National Formosa University, Taiwan

Transition metal nitride coatings based on Cr, Ti and Al, such as AlTiN, AlCrN and AlCrSiN, have been used as protective coating materials of cutting and forming tools due to their high hardness and thermal stability. In this study, AlCrSiN and AlTiCrSiN coatings were deposited onto high-speed steels and tungsten carbide tools using AlTi, TiSi, Cr and ternary AlCrSi alloy targets in a Cathodic-arc evaporation (CAE) system. Optimal design of interlayers of the AlCrSiN and AlTiCrSiN can offer an efficient way of controlling residual stress, improving adhesion strength and enhancing toughness. During the coating process of AlCrSiN and AlTiCrSiN, AlCrN and AlTiN were deposited, respectively, as interlayers with different structures to control residual stress, toughness and adhesion strength between the coatings and substrates. By controlling the different interlayers and negative bias voltages, the AlCrSiN and AlTiCrSiN possessed different microstructures and mechanical properties. The microstructure of the deposited coatings was investigated by field emission scanning electron microscope (FE-SEM) and field emission gun high resolution transmission electron microscope (FEG-HRTEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction was used to characterize the microstructure and phase identification of the coatings. Mechanical properties, such as the hardness and young's modulus, were measured by means of nanoindention. The adhesion strength of the coatings was evaluated by a standard Rockwell indentation test. In order to evaluate the impact fatigue behavior of the coated samples, an impact test was performed using a cyclic loading device with a tungsten carbide indenter as an impact probe. For the cutting experiment, 316L stainless steel was machined by the coated end mills under oil mist condition using a

CNC milling machine. The design of AlCrTiSiN coatings were anticipated to increase the hardness, toughness, thermal stability and impact resistance by optimizing the interlayers and bias condition of the deposition.

Keywords : Mechanical property; Cutting; Hard coating; Interlayer

3:20pm **B4-4-WeA-5 Erosion, Corrosion Resistance and Hydrophobicity of Nano-layered and Multi-layered Nitride Coatings***, **Qi Yang**, L Zhao, P Patnaik,* National Research Council of Canada, Canada

Nano-layered CrTiN, CrTiAlN, CrAlTiN, multi-layered CrAlTiN-CrN and CrAlTiN-AlTiN coatings were deposited on 17-4 PH stainless steel substrate by the cathodic arc evaporation technique. Solid particle erosion tests were performed to investigate their erosion resistance. All of these coatings, CrAlTiN and CrAlTiN-AlTiN coatings in particular, demonstrated higher resistance to solid particle erosion at both low and high impingement angles when compared to the single layered CrN coating. For example, the mass erosion rates of the nano-layered CrAlTiN coating were less than 1/3 and 1/7 of the corresponding erosion rates of the CrN coating at 30° and 90° respectively. The excellent erosion performance of the coatings was attributed to the improved hardness. Potentiodynamic polarization tests of the coatings in 3.5% NaCl aqueous solution indicated that these coatings had higher corrosion potentials and much wider passive ranges with comparable or lower current densities, when compared to 17-4 PH. Water contact angle measurements illustrated that the nitride coatings also had good hydrophobic characteristics.

3:40pm **B4-4-WeA-6 Microstructure and Thermal Stability of Al-rich Ti-Al-Mo-N Protective Coatings***, **Christina Wüstefeld**,* Institute of Materials Science, TU Bergakademie Freiberg, Germany*; M Motylenko,* Technische Universität Bergakademie Freiberg, Germany*; S Berndorf,* Institute of Materials Science, TU Bergakademie Freiberg, Germany*; M Pohler, C Czettl,* CERATIZIT Austria GmbH, Austria*; D Rafaja,* Technische Universität Bergakademie Freiberg, Germany

Ti-Al-N coatings are known as protective coatings in metal cutting applications. Further improvements of the mechanical properties and thermal stability of Ti-Al-N coatings are aspired by the addition of alloying elements like tantalum, niobium or molybdenum and by the adjustment of the microstructure via the deposition parameters. In this study, the Mo content and the bias voltage were varied in order to investigate the impact on the microstructure and thermal stability of Al-rich Ti-Al-Mo-N coatings. The coatings were deposited using cathodic arc evaporation (CAE) in nitrogen atmosphere from $Ti_{32}Al_{65.5}Mo_{2.5}$ and $Ti_{28}Al_{62}Mo_{10}$ targets at different bias voltages that ranged between -40 V and -120 V. In order to study the influence of the Mo addition on the thermal stability, selected samples were annealed in argon atmosphere up to 1000 °C. The as deposited and annealed Ti-Al-Mo-N coatings were characterized by using a combination of X-ray diffraction and transmission electron microscopy (TEM) with high resolution and in scanning mode. TEM in scanning mode was supplemented by electron energy loss spectroscopy and energy dispersive spectroscopy.

The microstructure of the coatings was described in terms of the chemical and phase composition, stress-free lattice parameters of the fcc-phase, macroscopic residual stresses as well as the sizes and preferred orientations of fcc crystallites. It could be shown that the bias voltage can be used to control the fractions of fcc-(Ti,Al,Mo)N and wurtzitic AlN in Al-rich Ti-Al-Mo-N coatings. The correlation between the microstructure characteristics, the parameters of the deposition process and the hardness is discussed.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B6-ThM

Coating Design and Architectures

Moderators: Shou-Yi Chang, National Tsing Hua University, **Paul Heinz Mayrhofer**, Institute of Materials Science and Technology, TU Wien, Austria

8:00am **B6-ThM-1 The Mechanical and Tribological Properties of Boron Based Films Grown by HiPIMS Under Different N_2 Contents***, A Keleş, **Ihsan Efeoğlu**, Y Totik,* Ataturk University, Turkey

The cubic phase of boron nitride (c-BN) has significant technological potential for thin film applications. It is generally compared with diamonds due to c-BN properties. c-BN is a semi-stable, high temperature and high pressure (HPHT) stable phase with high strength covalent bond and the second highest hardness. However, c-BN film has low adhesion at the interface due to high compressive internal stress. To overcome this problem, c-BN films were coated with HiPIMS-CFUBMS under three different N_2 contents (2.5 sccm, 3 sccm, 3.5 sccm). Before deposition of c-BN film, Ti-TiN-TiB_2-TiBN-TiBCN graded composite layers were coated for improving the adhesion. The structural properties were identified using SEM. The chemical properties were determined using XPS. The c-BN content and internal compressive stress were calculated using FT-IR. The mechanical properties were carried out by microhardness tester and scratch tester. The tribological properties were experimented with pin-on-disc tribometer. The maximum hadness (45GPa) and minimum critical load (Lc»69N) values were obtained from the lowest N_2 content (2.5sccm). Also, the minimum friction coefficient value was 0.622. The results showed that c-BN films coated with HiPIMS is very up-and-coming.

8:20am **B6-ThM-2 Peculiar Oscillations in Nano-scale AlN/TiN and Other Nitride-based Superlattices***, **Nikola Koutna**,* Institute of Materials Science and Technology, TU Wien, Austria*; P Řehák,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic*; Z Zhang,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; M Černý,* Central European Institute of Technology, CEITEC VUT, Brno University of Technology, Czech Republic*; M Bartosik,* Institute of Materials Science and Technology, TU Wien, Austria*; M Friák, M Šob,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; D Holec,* Department of Physical Metallurgy and Materials Testing, Montanuniversität Leoben, Austria

Superlattices with layer thicknesses of only a few nm cannot be simply understood based on the knowledge of their monolithic building components. Different phases and/or their mutual orientation together with the presence of interfaces may lead to peculiar physical phenomena, such as partial structural transformations, superhardening or supertoughening effects.

This talk centers around an AlN/TiN multilayered system, combining materials that are very popular in industrial applications. Though considerable experimental as well as modelling efforts have been devoted to AlN/TiN system, the atomic-scale effects of the interface are not fully understood. Our ab initio calculations reveal interplanar spacing oscillations stemming from the presence of the interface and the corresponding changes in the electronic structure. The character of these oscillations differs significantly in each material–AlN and TiN–based on the superlattice-forming phases (metallic TiN vs. semiconducting AlN, or cubic vs. hexagonal AlN) and their orientation (e.g., (001) vs. (111)), influencing the critical distance from the interface above which the oscillations disappear. The oscillatory behaviour of atomic displacements have also important consequences for elastic constants as well as the cleavage properties in terms of theoretical critical stress and energy for brittle cleavage. Our Density Functional Theory calculations are corroborated with observations from high resolution transmission electron microscopy. Consequently, atomistic reasons for superior mechanical properties of AlN/TiN multilayered systems are proposed. Our findings are compared with the relevant predictions for other superlattice architectures containing (meta)stable phases of transition metal nitrides.

8:40am **B6-ThM-3 Impact Fatigue and Mechanical Properties of AlTiCrN and AlTiCrSiN Hard Coatings with Optimal Design of Interlayers***, **Yu-Ju Yang**, Y Chang, S Weng,* National Formosa University, Taiwan

Optimal design of interlayers of a hard coating can offer an efficient way of controlling residual stress, improving adhesion strength and enhancing toughness. Transition metal nitrides, such as AlTiCrN, have been used as protective hard coatings due to their high hardness and high resistance to high temperature oxidation. In this study, AlTiCrN and AlTiCrSiN coating was deposited by cathodic-arc evaporation (CAE). During the coating process of AlTiCrN and AlTiCrSiN, TiN and CrN were deposited, respectively, as interlayers with different graded structures to control residual stress, toughness and adhesion strength between the coatings and substrates. The microstructure of the coatings was characterized by using a field emission scanning electron microscope (FE-SEM), equipped with an energy-dispersive x-ray analysis spectrometer (EDS). Glancing angle X-ray diffraction (XRD) was used to characterize the microstructure, phase identification and residual stress. The chemical composition was also evaluated. The thickness and alloy content of the deposited coating were correlated with the evaporation rate of cathode materials. Mechanical properties, such as the hardness and elastic modulus, were measured by means of nanoindention and Vickers hardness measurement. To study the correlation between impact fracture resistance and hardness/elastic modulus ratio of the deposited coatings, an impact test was performed at 500 ^oC using a cyclic loading device with a tungsten carbide indenter as an impact probe. The results indicated that all the AlTiCrN and AlTiCrSiN coatings exhibited (Al,Ti,Cr)N solid solution phases with NaCl-type structure. The design of AlTiCrN hard coatings with optimal designed interlayers of CrN and AlTiCrN/CrN can decrease residual stress, enhance hardness and toughness, which were effective to elimination of cracking of hard coatings. The AlTiCrN and AlTiCrSiN hard coatings with multilayered interlayers of CrN and AlTiCrN/CrN possessed the best resistance to plastic deformation and the highest impact fatigue resistance. The AlTiCrN and AlTiCrSiN hard coatings with optimal design of interlayers can be good candidates for piercing, punching and molding applications.

9:00am **B6-ThM-4 Improvement of CrMoN/ SiN_x Multilayered Coatings on Mechanical and High Temperature Tribological Properties***, **Wei-Li Lo**, L Yeh-Liu, J Lee, J Duh,* National Tsing Hua University, Taiwan

In this study, CrMoN/SiN_x multilayered coatings were deposited by controlling the shutter-open time of two sputtering guns in a radio frequency magnetron sputtering system. CrMoN/SiN_x thin films with different bi-layer periods were fabricated on both Si-wafer and Inconel-718 substrates. The chemical composition of as-deposited CrMoN/ SiN_x coatings were obtained by a field emission electron probe micro-analyzer (FE-EPMA). The confirmation of multilayered structure and crystallization characterization were carryied out using a transmission electron microscope (TEM). The phases of the coatings were analyzed by a grazing incidence X-ray diffraction (XRD). Mechanical and high-temperature tribological properties were estimated using a nano-indenter and a high-temperature tribometer (ball-on-disc), respectively.

The grain refinement phenomenon was verified using XRD peak broadening at high angles, indicating inhibition in the column structure and the formation of an amorphous phase. The CrMoN/SiN_x multilayered coatings exhibited high-temperature tribological properties for a specific bi-layer period, which was attributed to the multilayer strengthening mechanism. Multilayered structure provided enormous benefit to COF improvement, which was reduced by 50% of the value of CrMoN. In the meanwhile, the toughening effect of the multilayered structure design also improved the wear resistance ability of the coatings. Moreover, the best bi-layer period was identified, resulting in favorable mechanical and high-temperature tribological properties. Eventually, a CrMoN/SiN_x multilayer coating with enhanced high-temperature characteristics was demonstrated and discussed in this study.

9:20am **B6-ThM-5 Tuning the Hardness–toughness Relationship by Combining MoN with TaN***, F Klimashin, N Koutna, L Lobmaier,* TU Wien, Institute of Materials Science and Technology, Austria*; D Holec,* Montanuniversität Leoben, Austria*; **Paul Heinz Mayrhofer**,* TU Wien, Institute of Materials Science and Technology, Austria

Recently we showed that cubic-structured Mo–N and Ta–N exhibit an inherent driving force for vacancies at the nitrogen and metal sublattice, respectively. To shed light on their interaction and effects on structural evolution and mechanical properties within the ternary system Mo–Ta–N, we have synthesised coatings by means of reactive magnetron sputtering with varying nitrogen partial pressure. Low nitrogen partial pressures, resulting in high concentration of vacancies on the N sublattice, allow one to stabilise single-phase cubic-structured solid solutions up to a high metal fraction of Ta of x = Ta/(Mo+Ta) of at least 0.76. These solid solutions form with vacancies predominantly at the nitrogen sublattice, with increasing vacancy concentration upon increasing x. Furthermore, with increasing x to 0.56, also the compressive residual stresses increase to -2 GPa, the hardness increases to 36 GPa, and the fracture toughness increases to 7 MPa√m. Schottky defects, energetically favoured at higher tantalum concentration (at least up to $x = 0.76$), cause in turn the relaxation of compressive residual stresses to -1.3 GPa and reduction in hardness to 29 GPa and fracture toughness to 5 MPa√m. On the contrary, high nitrogen partial pressures favour vacant sites on the metal sublattice of cubic-structured solid solutions, which are the major constituent in these dual-phased coating. The hardness of these dual-phase coatings is mainly determined by the fraction of the coexisting hexagonal phase, which appears to be the harder constituent. However, neither hexagonal phases nor vacancies at the metal sublattice are desirable when aiming to combine high hardness with high fracture toughness in this Mo–Ta–N system. The fracture toughness would be reduced to 2.5 MPa√m. The binary γ-$MoN_{0.89}$ with partially ordered vacancies on metal and non-metal sublattices possesses the highest toughness among all coatings studied with 8 MPa√m, while showing a moderate compressive residual stress of -2 GPa and hardness of 28 GPa. Our findings show that by combining materials with a driving force for metal or nitrogen vacancies, both routes of structural evolution can be designed, allowing to tune their mechanical and elastic properties.

9:40am **B6-ThM-6 Microstructure, Mechanical and Tribological Performance of Complex TiAlTaN-[TiAlN/TaN$_n$] Coatings: Understanding the Effect of Volume Fraction***, Elbert Contreras, J Cortínez,* Universidad de Antioquia, Colombia*; A Hurtado,* Centro de Investigación en Materiales Avanzados CIMAV, Mexico*; M Gómez,* Universidad de Antioquia, Colombia

Recent studies have shown that by modifying the coatings architecture it is possible to obtain significant improvements in their mechanical and tribological properties. In the present work four complex TiAlTaN-[TiAlN/TaN$_n$] coatings were deposited, varying the volume fraction of the top quaternary coating (TiAlTaN) and the base multilayer coating (TiAlN/TaN) with percentages of: 20/80, 40/60, 60/40 and 80/20, and evaluating their effect on mechanical and tribological performace of the complex coatings. The cross-sectional images obtained by FIB-SEM showed the interface between each of the constituent monolayers, a well-defined columnar structure was also observed for the TiAlN/TaN multilayer coating, while in the quaternary TiAlTaN coating a refinement was observed in the columns with denser and compact structures. High-resolution TEM analysis revealed well-formed multilayer composites with very smooth layers. The complex TiAlTaN-[TiAlN/TaN$_n$] coatings did not exhibited a significant difference in their crystalline structure, however, once calculating the residual stresses by XRD, it was found that by increasing the volume fraction of the multilayer in the coatings there is a decrease in the compressive residual stresses. Regarding the mechanical properties, it was possible to observe an increase between 20-25% when increasing the volume fraction of the multilayer, as well as an increase in resistance to plastic deformation (H^3/E^2), fracture toughness and in the adhesion of complex architecture coatings. With respect to tribological properties, TiAlTaN-[TiAlN/TaN$_n$] coatings exhibited lower friction coefficients and wear rates compared to constituent monolayers. Using cross-section FIB it was possible to observe initial deformation in the constituent layers followed by the propagation of cracks along the interfaces between TiAlTaN, TiAlN and TaN layers, in nanoindentation tests, scratch tests and tribological tracks.

10:00am **B6-ThM-7 Plastic Deformation in Transition-Metal Nitrides and Carbides via Density-Functional Molecular Dynamics***, Davide Sangiovanni,* Linköping University, Sweden, Ruhr-Universität Bochum, Germany **INVITED**

Hard refractory transition-metal nitrides and carbides (TMN and TMC) possess unique combinations of outstanding physical and mechanical properties. As most ceramics, however, TMN and TMC are typically inherently brittle. Recent theoretical and experimental results have demonstrated that TMN can be made *bothhard* (~20 – 25 GPa) *and ductile* via manipulation of electronic structures and control of phase stability. This surprising finding addressed a long-standing question in materials science on whether hardness and ductility are necessarily mutually exclusive properties in a single-crystal ceramic phase. Nevertheless, it is still puzzling how high hardness and excellent ductility may coexist given that the two properties are affected in opposite manner by plastic deformation.

This seminar will be divided in three parts. (*i*) I will first describe density-functional theory results to explain the effects induced by valence electron concentrations and phase stabilities on toughness of TMN and TMC; (*ii*) Then, I will show the results of finite-temperature *ab initio* molecular dynamics (AIMD) simulations of tensile, shear deformation, and nanopillar compression to clarify the atomistic pathways with associated changes in electronic structures responsible for brittleness (TiN and VN) vs. supertoughness (VMoN, VN_x); (*iii*) Finally, I will give an overview of AIMD simulations for slip system activation/quenching as a function of temperature and pressure to demonstrate unusual non-Schmid behavior in TMC. All first-principles results will be discussed in comparison with, and supported by, experimental findings.

10:40am **B6-ThM-9 Phase Evolution and Mechanical Properties of Isostructural Decomposing $W_{1-x}M_xB_2$ Thin Films***, Vincent Moraes, L Zauner,* TU Wien, Institute of Materials Science, Austria*; H Bolvardi,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; P Polcik,* Plansee Composite Materials GmbH, Germany*; H Riedl, P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

The increasing demand in various industrial applications calls for a target-driven development of protective coatings with exceptional properties. Therefore, transition metal nitrides have been studied and developed extensively. However, the exploration of new protective coating systems is required to meet upcoming challenges not only in machining applications. A rather new promising class of materials – to be used as protective thin films – are borides. Especially, multinary borides are rather unexplored compared to their nitride-based counterparts. Coherent phase separation effects of supersaturated single-phased structures such as age hardening in $Ti_{1-x}Al_xN$ based thin films was a key-factor for the success being nowadays one of the most important material combination in thin film industries. The formation of coherent domains through spinodal decomposition ($Ti_{1-x}Al_xN$ into TiN- and AlN-rich cubic domains) allows for significant strengthening effects at elevated temperatures (for example, as obtained during application). Transferring the concept of two competing phases from nitrides to borides is a promising approach to find new materials with outstanding properties already in the as deposited state. Different ab initio and experimental studies [1-3] already showed that WB_{2-z} thin films preferable crystallize in their metastable α-AlB_2 modification (space group 191), being an excellent origin for ternary alloying concepts considering the decomposition to its stable ω-W_2B_{5-x} configuration (space group 194).

In this study, we experimentally investigated the structural and mechanical evolution for selected ternary $W_{1-x}M_xB_2$ based thin films concerning spinodal decomposition. Especially, not only the effect of coherent phase separation on the hardness but also fracture toughness has been correlated with temperature. This aspect is highly important, as most of the α-AlB_2 structured diborides (e.g. TiB_2, ZrB_2, or CrB_2) suffer extremely low damage tolerance. In addition, the phase evolution with respect to structural defects (e.g. metal or boride vacancies) was also investigated by ab initio based calculations.

Keywords: W_2B_{5-x} based diborides; multinary borides; mechanical properties; coherent phase separation;

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11:00am **B6-ThM-10 Van der Waals Layer Promoted Heteroepitaxy in Sputter-deposited Thin Films***, Koichi Tanaka, P Arias, M Liao, Y Wang, H Zaid, A Aleman, M Goorsky, S Kodambaka,* University of California, Los Angeles, USA

We demonstrate that the crystallinity of sputter-deposited thin films can be significantly improved using two-dimensional (2D) van der Waals (vdW) layered materials as the buffer layers on substrates. Using hexagonal boron nitride (hBN) (a = 0.250 nm and c = 0.667 nm) as the 2D vdW buffer layer, we grow trigonal-structured Ta_2C (a = 0.310 nm and c = 0.494 nm) thin films of desired thickness (t = 17 ~ 75 nm) on Al_2O_3(0001) substrates via ultra-high vacuum direct current magnetron sputtering of TaC compound target in 20 mTorr pure Ar gas atmospheres at 1373 K. hBN layers are deposited via pyrolytic cracking of borazine (~600 L) onto Al_2O_3(0001) substrates at 1373 K. The as-deposited Ta_2C films are characterized *in situ* using Auger electron spectroscopy and low-energy electron diffraction and *ex situ* using X-ray diffraction (XRD) and transmission electron microscopy (TEM) based techniques. For the same Ta_2C film thickness, the notable differences in the layers deposited on hBN-covered Al_2O_3(0001) compared to those grown on bare substrates are: observation of 6-fold symmetric LEED pattern, significantly stronger (20x´) 0002 reflection intensity in ω-2θ XRD scans, and observation of Laue oscillations around the 0002 peak. Furthermore, we show that inserting hBN layers at regular intervals results in highly-0002-oriented growth and suppression of polycrystallinity in thicker Ta_2C films.

11:20am **B6-ThM-11 Improvement of Tribological Properties for Hard Coatings by Stress Control**, ***Tianmin Shao,*** State Key Laboratory of Tribology, Tsinghua University, China

For the application of hardcoatings, stress level in coating/substrate systems is one of the main factors influencing their tribological properties. In many applications, effective control of stresses is of great importance for the performance and working life of hard coatings. Generally, the stress inside coatings subjected during service is a combination of external stress and intrinsic stress. The external stress is mainly determined by the applied working load, and the intrinsic stress depends on the coating material, the structure of coating, property mismatch between coating and substrate, coating production process, etc. In this presentation, control of intrinsic stress by properly design of coating/substrate system is studied. As examples, studies on stress control by textured coating technique and design of layered structures are introduced. Tribological properties of several hard coatings are experimentally studied and the results are discussed based on stress analysis. Results show that both textured coating and layered structure can be used for stress control of coating/substrate systems, and eventually improving their tribological properties.

Keywords: stress control; tribological property; hard coating; textured coating; layered structure

11:40am **B6-ThM-12 Is WB_{2-z} a Proper Base System for Designing Ternary Diboride based Thin Films?**, ***Helmut Riedl***, *V Moraes, C Fuger, H Euchner, R Hahn, T Wojcik,* TU Wien, CDL AOS at the Institute of Materials Science, Austria; *M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein; *P Polcik,* Plansee Composite Materials GmbH, Germany; *P Mayrhofer,* TU Wien, Institute of Materials Science, Austria

Future tasks in many different fields of academia and industry are directed towards environmental sustainability, and hence the application of ultra-stable materials featuring novel properties. A rather new and highly promising class of thin film materials are borides. Especially, transition metal borides (TMBs) exhibit a tremendous potential to be applied in various applications ranging from wear and corrosion resistant coatings, to superconductive thin films, or as superhard and extremely stable protective layers in diverse fields of engineering. In contrast to classic diborides – such TiB, ZrB_2,WB_2, or ReB_2, which has been theoretically predicted to be the most incompressible material exceeding the properties of diamond – are ternary or even multinary diborides (e.g. $W_{1-x}M_xB_2$) relatively unexplored. Based on atomistic modelling studies [1,2] (Density Functional Theory calculations) is the stabilization of ternary diborides dominated by two hexagonal competing structure types – α–AlB_2-prototype (SG-191) vs. ω-W_2B_{5-x}-prototype (SG-194) – as well as structural defects (especially vacancies). These facts emphasize distinct difficulties for PVD based synthesis of ternary diboride thin films.

Within this study, we want to address the challenges in depositing ternary diborides in a prototype based on α-$W_{1-x}M_xB_2$ solid solutions, applying non-reactive sputtering processes, whereas M represents different transition metals such as Ta or Ti [2]. Due to the strong tendency of WB_2 to be stabilized through structural defects in the AlB_2 structure type – exhibiting distinct advantages concerning the relatively low ductility of TMBs in general – it can be an excellent base system for studying various alloying concepts utilizing physical vapour deposition (PVD) techniques. To gain an in-depth insight on the specific effects of selected transition metals on α structured $W_{1-x}M_xB_2$ coatings, we correlated the synthesis parameter with structure property relationships applying a set of high-resolution characterization techniques as well as micro-mechanical testing methods – also after exposing to diverse aggressive- environments in terms of oxidation and thermal treatments.

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Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-1-ThA

CVD Coatings and Technologies I

Moderators: Kazunori Koga, Kyushu University, Japan, **Francis Maury**, CNRS-CIRIMAT

1:20pm **B2-1-ThA-1 Impact of HfO_2 as a Buffer Layer on the Electrical and Ferroelectric Memory Characteristics of Metal/Ferroelectric/High-K/Semiconductor Gate Stack for Nonvolatile Memory Applications***, R Jha, P Singh,* ***Manish Goswami,*** Indian Institute of Information Technology Allahabad, India*; B Singh,* Park Systems, India

For the proposed work, the electrical properties of metal-ferroelectric-insulator-silicon (MFeIS) capacitors with $Sr_{0.8}Bi_{2.2}Ta_2O_9$ (SBT) ferroelectric film deposited on HfO_2/Si substrate has been investigated. The SBT film was deposited by RF sputtering and HfO_2 film by plasma enhanced atomic layer deposition (PEALD). The structural characteristic of the deposited ferroelectric and dielectric films was obtained using X-ray diffraction and multiple angle ellipsometric analysis. Metal/Ferroelectric/Silicon (MFeS), Metal/Ferroelectric/Metal (MFeM), Metal/Insulator/Silicon (MIS) and Metal/Ferroelectric/Insulator/Silicon (MFeIS) structures were fabricated to obtain the electrical and ferroelectric properties. MFeIS structure with 10 nm buffer layer shows the improved memory window of 5 V as compared to the 3.07 V in the MFeS structures. $MFeI_{(10\ nm)}S$ structure even show endurance higher than 10^{12} read/write cycles and data retention for more than 8 hours. The effect of thickness and annealing temperature of buffer layer has also been investigated. The improvement in remnant polarization and coercive field due to the introduction of high-K layer has also been studied and compared with previous results .

1:40pm **B2-1-ThA-2 Studies on Properties and Cutting Performance of Al-rich AlTiN Coating with Controlled Orientation via LP-CVD***,* ***Yasuki Kido****, A Paseuth, S Okuno, S Imamura,* Sumitomo Electric Hardmetal Corp., Japan

Al-rich AlTiN is one of the important hard coatings for cutting tool. Among them, cubic phase AlTiN (c-AlTiN) comprising c-Al(Ti)N/c-Ti(Al)N nano-lamellae structure with high Al content and controlled orientation via LP-CVD has been modern coating due to high hardness and strength, compared to conventional CVD coating also AlTiN by PVD. The aim of this study is to investigate the effect of c-AlTiN coated carbide tools, as a function of component (Al/Ti ratio) and orientation, on mechanical and thermal properties also cutting performance. Deposition of c-AlTiN with controlled component and orientation was conducted by LP-CVD using AlCl3-TiCl4-NH3 precursor system. High-resolution transmission electron microscopy revealed formation of c-AlN and c-TiN-rich domains in nanometer scale. The c-AlTiN coating showed high hardness and compressive stress with adhesion by indentation technic, X-ray diffraction and scratch test. Also thermal property was measured. Furthermore, a cutting test for cast iron milling was performed with different kinds of component and orientation c-AlTiN coating on carbide tools.

2:00pm **B2-1-ThA-3 Effects of Al Content and Growth Orientation on Mechanical Properties of AlTiN Coatings Prepared by CVD Method***,* ***Kosuke Yanagisawa****, T Ishigaki, H Nakamura, H Homma,* Mitsubishi Materials Corporation, Japan

AlTiN coatings with high aluminum content have attracted attention due to its beneficial properties such as high oxidation resistance and age hardening effect on metal cutting. It is well-known that conventional AlTiN coatings are deposited by PVD method and the maximum aluminum content Al/(Al+Ti) is limited to lower than 0.67 to maintain a single phase cubic. Otherwise, in the range of aluminum content Al/(Al+Ti) higher than 0.67, they contain hexagonal phase which has lower hardness.

In this work, (111)- and (100)- oriented cubic AlTiN coatings with aluminum content higher than 0.67 were prepared on cemented carbide substrates by CVD method. Microstructure of the deposited coatings was observed by scanning electron microscopy, and the crystallographic orientation of these coatings was examined by X-ray diffraction analysis. Additionally, the hardness of these coatings was measured using nanoindentation and crack resistance property was evaluated by crack length induced by Vickers indentation, respectively.

From SEM observation, all of these coatings had columnar microstructures which contained self organised nano-lamellae structures in grains. Nano-lamellae structure in (100)-oriented coatings had a tendency to be smaller periods of the compositional fluctuation compared with those of (111)-oriented coatings, despite the almost same composition. As for the mechanical properties, the coatings with higher aluminum content or preferred (111) orientation showed higher hardness and higher crack resistance property. Thus, it was suggested that the hardness or crack resistance property of coatings was correlated to not only aluminum content but also the morphology of nano-lamellae structure.

One of possible explanation for the higher hardness, the deforming energy caused by indentation was dissipated by nano-lamellae structure. This effect is similar to a pinning effect for the propagation of the dislocations at interfaces of a multilayered coating. Regarding the superior crack resistance, it was attributed to crack deflection at the nano-lamellae structure.

Besides, these coatings were tested for the dry milling operation of 42CrMo4 steel blocks. It was indicated that CVD – AlTiN coatings with higher aluminum content showed superior wear and thermal crack resistance. On the other hand, the difference of coating orientation did not affect to the cutting results in this work.

2:20pm **B2-1-ThA-4 Thermal Crack Network Formation in CVD TiCN/α-Al_2O_3 Coatings***,* ***Nina Schalk****, R Stylianou, M Gassner,* Montanuniversität Leoben, Austria*; D Velic, W Daves, W Ecker,* Materials Center Leoben Forschung GmbH, Austria*; M Tkadletz,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria*; C Mitterer,* Montanuniversität Leoben, Austria

TiCN/α-Al_2O_3 coatings grown by thermally activated chemical vapor deposition on cemented carbide substrates typically exhibit a crack network as a result of the different thermal expansion coefficients (TEC) of coating and substrate material. Thus, the present work focuses on the investigation of these thermal cracks and on strategies to avoid them. The thermal cracks in industrially applied TiCN/α-Al_2O_3 coatings were studied in different conditions, i.e. in as-deposited state, after post-treatment by wet-blasting and annealing as well as after face turning, by scanning electron microscopy techniques. While wet-blasting results in closure of the thermal cracks near the coating surface due to the introduction of compressive stresses, annealing and turning lead to a relaxation of these stresses and thus in the reappearance of the cracks. In an attempt to avoid the formation or to reduce the density of cracks, TiCN/α-Al_2O_3 coatings were deposited on a series of cemented carbide substrates with cobalt contents of 6, 7.5, 10, 12.5 and 15 wt.%. The determination of the TEC of both, substrates and coating yielded a decreasing mismatch of the TECs with increasing cobalt content. At the highest cobalt content, no cracks and only low tensile stresses are observed in the coating. Decreasing the cobalt content yields first a tensile stresses maximum, followed by decreasing tensile stresses at even lower cobalt contents as a result of stress relaxation due to promoted crack formation. Finally, finite element simulations of the residual stresses in the coating after deposition, considering different crack distances, corroborate the experimental results.

3:00pm **B2-1-ThA-6 Structural and Piezoelectric Properties of Chemical Vapor Deposited AlN Films on Metallic Substrates***,* ***Juan Su****, M Pons, F Mercier, D Chen, R Boichot,* Université Grenoble Alpes, CNRS, France

To monitor the state of stress and damage in cutting tools or critical equipment working under extreme conditions such as high temperature, high pressure or aggressive chemical environment, the strongly textured AlN as a piezoelectric layer was successfully deposited on metals by Chemical Vapor Deposition (CVD) method. Low temperature textured TiN by CVD from $TiCl_3$-H_2-NH_3 system or AlN by Atomic Layer Deposition (ALD) is applied as a buffer layer to avoid the instability of metal substrates in CVD reactor during growth and decrease the huge mismatch between substrates and AlN layer. A design of experiment (DOE) is used to analyze the influence of 7 main process parameters and find a suitable experimental condition for depositing dense, covering and textured AlN. The morphology, XRD results and piezoelectric coefficient d_{33} are compared and analyzed. Unexpectedly, the results show that (200) textured TiN is a good buffer layer to obtain (002) textured AlN on WC-Co. On the contrary, the AlN with the thickness of 90 nm deposited by ALD is the best buffer layer for TZM. At last, the relationship between texture coefficient and d_{33} is studied considering 10 different orientations of AlN. It proves that when (002) texture coefficient is less than 2, d_{33} almost keeps constant at 0.14 pC/N, then it increases linearly to more than 2 pC/N while the theoretical bulk piezoelectric coefficient for AlN is around 6 pC/N.

3:20pm **B2-1-ThA-7 Aluminum Nitride Based Coatings for High Temperature Solar Receiver Systems***, **DanYing Chen**,* Université Grenoble Alpes, CNRS, France*; J Colas,* PROMES-CNRS, France*; J Su,* Université Grenoble Alpes, CNRS, France*; L Charpentier, M Balat-Pichelin,* PROMES-CNRS, France*; F Mercier, M Pons,* Université Grenoble Alpes, CNRS, France

There is a growing interest in concentrating solar power plants as electricity generation systems, whereby the sunlight is redirected and focused onto a receiver heated to high temperature. One of the challenges is to build the solar receiver which can work at temperatures near or higher than 1000 °C for optimizing the yield. Current candidate materials are metallic alloys such as Inconel, or bulk ceramics like silicon carbide, but their operating temperatures may be limited due to oxidation or mechanical problems. Aluminum nitride (AlN) coating, deposited by chemical vapor deposition at 1100 °C, was selected for its high thermal conductivity, low thermal expansion coefficient, high temperature stability and its oxidation resistance. It forms stable and protective alumina scales at temperatures higher than 1000°C. Oxide dispersion strengthened (ODS) FeCrAl alloy (Kanthal APMT), also alumina-forming, was chosen as a model substrate to study the potential of AlN coatings. Accelerated cyclic oxidation and high temperature emissivity measurements were performed in Odeillo solar furnace facilities (France), confirming the potential of aluminum nitride coatings as materials for high temperature central receivers. The AlN based multilayered system exhibits low degradation after 1500 h of oxidation at 1100 °C in air. The modelling and simulation of stresses during thermal cycles taking into account the creep and growth of the oxide layer are used to show the limits of use of these materials.

3:40pm **B2-1-ThA-8 Residual Stress and Quantitative Texture of CVD Al_2O_3 Coatings***, **Zhenyu Liu**,* Kennametal Inc., USA*; S Tan,* University of Pittsburgh, USA*; D Banerjee,* Kennametal Inc., USA

Conventional CVD coatings on cemented carbide are characterized by tensile stress, due to high temperature of deposition and thermal expansion mismatch between substrate and coating materials. The stress results in a mesh like cracking pattern in the coating, and may reduce toughness of coating leading to premature failure. It has been demonstrated that the tensile stress can be reduced, or reversed into compression by different postcoat blasting treatment. It is clear that postcoat blasting can reduce the extent of tensile stress in functional layer or even modified the stress state into compressive. At the same time, the residual stress of deposited coating and stress relieve during the high temperature caused by *in situ* heating during the metal-cutting practice, in another word, the stress situation in the coating, will affect the ultimate metal-cutting performance as well.

Anisotropic properties of crystal material make the texture of coated thin films a very important factor to affect the metal-cutting performance. Most of investigations on coating texture are determined by texture coefficient. There is still lack of the quantitative textural analysis of the tool coatings. With the aid of XRD/EBSD, the quantitative analysis of texture components can be determined then provide better evaluation on the highly textured coatings, such as Al_2O_3.

4:00pm **B2-1-ThA-9 Gas Source Chemical Vapor Deposition of Wafer-scale Mono- and few-layer MX_2 (M=W or Mo and X=S or Se) and Their Alloys***, **Mikhail Chubarov**, T Choudhury, D Reifsnyder Hickey, S Bachu, N Alem, J Redwing,* The Pennsylvania State University, USA **INVITED**

Transition metal dichalcogenides (TMD) like WS_2, WSe_2, MoS_2 and $MoSe_2$, when thinned to a monolayer (ML) thickness show direct bandgap, valley spin polarization, reasonable charge carrier mobilities and relatively high optical absorption; properties relevant to many applications. In addition to binary materials, alloys of TMD materials are also promising. It was reported that electronic transport properties are not dramatically deteriorated for the TMD alloys, and alloying allows for bandgap engineering over a wide range between 1.56 eV (794.8 nm) for $MoSe_2$ and 2.01 eV (590.4 nm) for WS_2. To push these materials towards practical applications, wafer-scale epitaxial growth of ML and few-layer (FL) films is necessary which can be achieved using CVD. In this study, to achieve ML and FL epitaxial layers of TMD materials and their alloys, we use gas source CVD and sapphire ((0001) α-Al_2O_3) as substrates.

For the growth we employ metal hexacarbonyls ($W(CO)_6$ and $Mo(CO)_6$) and hydrides (H_2S, H_2Se) as precursors diluted in hydrogen (H_2) carrier gas. Deposition temperature for this class of materials is in the range between 800 and 1000 °C at a pressure of 50 Torr for sulfides and 200 Torr for selenides. For the growth of binary compounds, a previously developed multistep growth process was employed while for the alloys, a single step was implemented to minimize routes for the formation of compositional gradients in the resulting layers.

As a result, we obtained ML and FL films of TMD materials. Acquired samples showed epitaxial relation with the substrate, high intensity photoluminescence and, for the alloys, composition control was achieved over a wide range as determined using X-ray photoelectron spectroscopy. Growth of WS_2 films resulted in growth of epitaxial ML films ((10-10)WS_2//(10-10)α-Al_2O_3) with in plane twist of 0.1°, room temperature photoluminescence (PL) showed emission maximum at 2 eV and width of 0.04 eV with pronounced exciton and trion components as well as defect-bound exciton emission. Domain size and distribution of antiphases were studied using transmission electron microscopy (TEM). This showed a relatively low fraction of isolated antiphase regions.

$WMoS_2$ alloys showed variation in the PL peak position as well as a change in the Raman scattering spectra which can be correlated with the composition of the film. Microstructure of the films was studied using TEM that showed no distinct segregation of the metal atoms when continuous flows of metal precursors were used.

Further details on the growth and characterization of MoS_2, WSe_2 and $MoSe_2$ will be presented along with the results obtained from ternary alloy growth and characterization.

4:40pm **B2-1-ThA-11 The Effect of Dopants and Bilayer Period on Microstructure and Mechanical Properties of CVD Ti(B,C)N Hard Coatings***, **Christina Kainz**, N Schalk, M Tkadletz, C Mitterer,* Montanuniversität Leoben, Austria*; C Czettl,* CERATIZIT Austria GmbH, Austria

The cutting performance of CVD TiN hard coatings can be improved by both, the alloying with additional elements, or through the application of a multilayered coating design. However, limited literature is available on the mutual influence of chemical composition and architecture on the properties of CVD Ti(B,C)N coatings. Thus within this work, a comparison of mono- and multilayered CVD hard coatings within the system Ti(B,C)N with a particular focus on their microstructure, mechanical properties and microscopic fracture behavior is presented. The coatings were grown onto cemented carbide substrates in an industrial-scale thermal CVD plant using BCl_3, CH_4, $TiCl_4$, N_2 and H_2 precursors. Transmission electron microscopy investigations showed a higher defect density and grain refinement in the ternary and quaternary coatings compared to binary TiN. X-ray diffraction confirmed the presence of the hexagonal TiB_2 phase embedded in the B-containing coatings within the face-centered cubic TiN or TiCN matrix. Nanoindentation revealed an increase of hardness with decreasing bilayer period for the multilayer coatings and the highest hardness (32.2±1.0 GPa) and Young's modulus (587±29 GPa) for the TiBCN monolayer coating. Finally, bending tests, performed with free-standing coating micro-cantilevers prepared by focused ion beam milling, provided insights into the effect of alloying and bilayer period on coating strength and toughness. This juxtaposition of different chemical compositions and architectures enables to identify the most promising coating for application in metal cutting.

Keywords: CVD, Ti(B,C)N, hard coatings, TEM, micromechanical testing

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-1-ThA

Hard and Multifunctional Nanostructured Coatings I

Moderators: Tomas Kozak, University of West Bohemia, **Helmut Riedl**, TU Wien, Institute of Materials Science and Technology

2:00pm **B5-1-ThA-3 Interfaces and Mechanisms: A Molecular Dynamics Approach to Fine Tuning Manipulation of Mechanical Properties***, **Alberto Fraile**, H Yavas, E Frutos,* Department of Control Engineering, Faculty of Electrical Engineering, Czech Technical University in Prague, Czech Republic*; T Huminiuc,* Engineering Science, Faculty of Engineering and the Environment, University of Southampton, Southampton, UK*; T Polcar,* Czech Technical University in Prague, Czech Republic

With the advent of more and more powerful supercomputers, Molecular Dynamics (MD) is playing today a capital role in the understanding of the deformation mechanisms at the atomic scale of all kind of materials under different scenarios. Many investigations have demonstrated that the peculiar features of nanoplasticity generated during indentation can be analyzed in detail by this technique.

Using MD we are constructing deformation-mechanism maps based on fundamental physical processes in the deformation of nanostructured materials. The knowledge for these processes comes from modelling the nanostructures at the atomic level by using atomistic simulations. The power of our approach is that it integrates the most important physics associated with deformation phenomena, in a self-consistent description of the effects of stress, interfaces and grain size on the mechanical properties in nanocrystalline structures, thereby avoiding the empiricism of other methods.

We have prepared different Zr/Nb layered systems (with different Nb/Zr geometries and/or structures) and indentation hardness close to the theoretical limits was measured for special cases. Then, our theoretical calculations were compared to the experimental results. Special attention was devoted to the effect of interlayers, grain boundaries, dislocation reactions as well as the effect of phase transitions in Zr.

The dominant deformation mechanism of metallic multilayered systems is the confined volume dislocation reactions, however, we also showed that there is a high possibility to control the deformation by tunning phase transformations at the nanoscale. This knowledge will open new doors to shed light into hidden features of the deformation and strengthening mechanisms guiding the design the next generation of metallic coatings and alloys.

2:20pm **B5-1-ThA-4 Preparation of Hard Yet Fracture Resistant W-B-C Coatings Using High Power Impulse Magnetron Sputtering***, **Pavel Soucek**, M Polacek, P Klein, L Zabransky, V Bursikova, M Stupavska,* Masaryk University, Brno, Czech Republic*; Z Czigany, K Balazsi,* Hungarian Academy of Sciences, Hungary*; P Vasina,* Masaryk University, Brno, Czech Republic

As the demands for the quality and speed of machining increase, the application of protective coatings on the used cutting tools becomes ever more important. Nowadays used ceramic protective coatings exhibit high hardness and toughness, however, they suffer from inherent brittleness. This can lead to a premature failure of the coating and of therefore of the cutting tool as a whole due to rapid crack propagation. Thus, a new generation of coatings combining hardness and moderate ductility is sought for.

Such a combination of seemingly mutually exclusive properties was recently predicted by ab-initio calculations in inherently nanolaminated X_2BC crystalline coatings, where X is a metallic element [1]. W_2BC system was found the most promising regarding its mechanical properties with predicted Young's modulus of ~ 470 GPa, B/G ratio of 1.91 and Cauchy pressure of 71 GPa. However, only a near zero negative value of its formation enthalpy of -0.16 eV/atom predicts problems with crystallization of this phase [1]. Indeed, previous works using mid-frequency pulsed DC sputtering did not report the formation of the crystalline W_2BC phase [2].

This contribution reports on the synthesis and comparison of W-B-C coatings sputtered from a compound W_2BC target using DCMS and HiPIMS, respectively. Different substrate temperatures up to 700°C were used in each case. The differences in the DCMS and HiPIMS deposition processes will be discussed. The microstructure of the coatings is investigated and is correlated to their mechanical properties. The fracture resistance and the deformation behaviour of the coatings will be discussed. Simultaneous achievement of high hardness and fracture resistance will be shown as well as the means of its achievement will be discussed.

This research has been supported by project LO1411 (NPU I) funded by the Ministry of Education, Youth and Sports of the Czech Republic.

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2:40pm **B5-1-ThA-5 Analytical Modelling of Misfit Dislocation Formation in Superlattice Coatings and its Effect on the Fracture Toughness***, **Antonia Wagner,*** TU Wien, Institute of Materials Science and Technology, Austria*; D Holec,* Montanuniversität Leoben, Austria*; M Todt,* TU Wien, Institute of Lightweight Design and Structural Biomechanics, Austria*; P Mayrhofer, M Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria

Coherently grown multilayer coatings with a bilayer period in the nanometer range exhibit a superlattice (SL) effect in mechanical properties like hardness and fracture toughness [1, 2]. While the superlattice effect in hardness is well described by the model after Chu and Barnett [3] based on dislocation plasticity, the fracture toughness enhancement in 'all-ceramic' SL coatings is not primarily governed by plasticity and the underlying mechanisms are less well understood.

The aim of the present work is to study the effect of the residual stress state in SL coatings on the fracture toughness. In general, extrinsic residual stresses (due to a mismatch of the coefficients of thermal expansion) and intrinsic stresses (stemming from the film growth process) contribute to the overall stress state. A major part of the intrinsic stresses, in turn, are coherency stresses, which originate from the epitaxial growth and the lattice mismatch of the film forming phases and the substrate material. While the thermal mismatch stresses are almost independent of the individual layer thicknesses, coherency stresses show a strong dependency when considering the formation of misfit dislocations. Up to a critical thickness of the layers, the misfit in the lattice parameters is accommodated by elastic strain, thereafter misfit dislocations form, preferably at the interface to the substrate or the previously deposited layer [4, 5].

We have calculated the dislocation density as a function of the layer thickness by an energy balance considering the strain energy of the system and the dislocation energy. An analytical model - with layerwise deposition of the individual layers including misfit dislocations - was developed to predict the stress state of superlattice systems as a function of the bilayer period. Finally, the fracture toughness and its dependence on the bilayer period was calculated taking into account the stress state, the intrinsic fracture toughness of the phases and the spatial variation of elastic properties of respective SL architectures.

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3:00pm **B5-1-ThA-6 The Electrical Response of PVD Deposited Nanocrystallited Carbon Film in Magnetic Field***, **Chao Wang**, J Guo, X Dai,* Institute of Nanosurface Science and Engineering, College of Mechatronics and Control Engineering, Shenzhen University, China

Nano-crystallited carbon film has gained much attentions due to its excellent electrical and mechanical properties, especially its magnetoresistance (MR) at room temperature. The novel electrical response of this film under external magnetic field shed light on a new-type carbon based magnetic sensing device. Recently, it is found that the MR performances of the film can be strongly improved by introducing Si as substrate instead of SiO 2 . Transport study implied that the film has high carrier density and ultra low mobility, which may be originated from the modulation effect of n-type doping substrate.

In this study, nanocrystallited carbon films were deposited on silica and N-type silicon substartes with plasma assisted PVD method. The nanocrystallited structure were observed through high resolution TEM and Raman spectra. The change of electrical resistances along with temperature and magnetic field strength were measured by using Quantum Design physical property measurement system(PPMS). The results showed that the nanocrystallied films showed large magnetoresistance at 300K, which is favorable for room temperature applications. The magnetic response behavior of the carbon films on different substrates were compared, which suggested that the n-silicon substrate can remarkably improved the magnetoresistacnce coefficient. The influences of gas flow, bias voltage, and deposition time on the structure, carrier density and magnetoresistance of the carbon films were invesitgated, and the transport mechanism of carriers in the films were discussed. We also found the large magnetoresistance of the film when using alternating current as stimulating source, when the largest rate of magnetoresistance can reach to 1000% per tesla at room temperature. This is ascribled to the inductive as well as spin-enhanced magnetoresistance effect due to the oriented graphene nanocrystalltes inside the semiconductive film matrix.

3:20pm **B5-1-ThA-7 Aluminium Nitride Based Piezoelectric MEMS: From Material Aspects to Low Power Devices***, **Ulrich Schmid**, M Schneider,* TU Wien - Institute of Sensor and Actuator Systems, Austria **INVITED**

In a compact introduction, I will motivate the benefits of piezoelectric thin films for MEMS and will give a short overview to state of art application scenarios on device level. Next, I will highlight latest results on the electrical, mechanical and piezoelectrical characterization of sputter-deposited aluminium nitride (AlN) including the impact of sputter parameters, film thickness and substrate pre-conditioning [1,2]. I will present the impact of doping of AlN with scandium, which leads to an increase of the moderate piezoelectric coefficient of AlN up to a factor of four. In a next step, these films are implemented into fabrication processes of cantilever-type MEMS devices. In combination with a tailored electrode design, resonators are realized featuring Q factors up to about 300 in liquids covering the frequency range of 1-2 MHz. This enables the precise determination of the viscosity and density of fluids up to dynamic viscosity values of almost 300 mPas [3]. Besides this application, such high Q factors are useful when targeting mass-sensitive sensors, thus paving the way to e.g. particle detection even in highly viscous media. Given the low increase in permittivity of ScAlN compared to AlN, another field of application for this material are vibrational energy harvesters, where the benefit of ScAlN compared to pure AlN is demonstrated [4]. Finally, I will present some selected results of ScAlN thin films within SAW devices ranging from high temperature applications to droplet manipulation in microfluidics [5].

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4:00pm **B5-1-ThA-9 Superamphiphobic Surface Produced by Femtosecond Laser Patterning and Pulsed Plasma Polymerization***, **Cheng-Wei Lin**,* Feng Chia University; Central Taiwan University of Science and Technology, Taiwan*; G Lu, X Chang, P Hsieh,* Feng Chia University, Taiwan*; C Chou,* Department of Surgery, Taichung Veterans General Hospital, National Yang-Ming University, Taiwan*; C Chung,* Central Taiwan University of Science and Technology, Taiwan*; J He,* Feng Chia University, Taiwan

The superamphiphobic surface may be widely applied, including medical devices, kitchen wares, architectures, and automotives, but is a challenging technique, with the unique characteristics of water and low surface tension liquids repelling, self-cleaning, anti-freezing and anti-bacterial activity. In this study, a dual-technique of surface modification by employing femtosecond laser patterning and pulsed plasma polymerization of octafluorocyclobutane was used to develop a superamphiphobic surface on the AISI 304 stainless steel substrate. Experimental results showed that the treated surfaces exhibited high water and oil contact angle, which may be attributed to nano/micro surface structure and low-surface-energy of fluorocarbon coating, as identified by SEM and FTIR analysis. In the steel wool scratch test, the superamphiphobic surface showed high mechanical durability even under harsh conditions. This indicates that such technique may have the potential in regulating surface properties of medical devices for different purposes.

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

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

BP-ThP-1 Low Stress AlTiN-Based Coating Systems*, C Charlton,* Kennametal Inc., USA*; **Joern Kohlscheen**,* Kennametal GmbH, Germany*; D Banerjee,* Kennametal Inc., USA

In this study, we deposited AlTiN coatings with reduced intrinsic stress for metal cutting applications. Stress management is important to maintain coating integrity during machining operations, especially at the cutting edge. Deposition was done in an industrial scale PVD unit using cathodic arc evaporation. Coating thickness was adjusted to about 3 µm. Al content in the metal fraction was varied between 60 and 70 atomic %. A reduction in compressive stress was achieved in four different ways: lowering bias voltage, layering of coating architecture, increasing pressure, and varying the cathode confinement ring system. Samples of cemented carbide and carbon steel strips were used for analyses. Chemical composition was measured by EDX. The microstructure of the obtained films was evaluated by x-ray diffraction (XRD). Stress was estimated using Stoney´s equation considering the resulting curvature of the partially coated steel strip. The values were validated using XRD peak shift measurements of the dominant cubic phase. It will be shown that a combination of bias and layer variation leads to an optimized ratio of low stress and wear resistance. Metal cutting data obtained by turning are showing that such coatings are able to outperform mono-layer coatings with higher stress.

BP-ThP-2 Multi-Target Co-Sputtering Deposition and Mechanical Properties of Ti-Zr-Based High-Entropy Alloy and Nitride Coatings*, **Shou-Yi Chang**, Y Hsiao,* National Tsing Hua University, Taiwan*; S Lin,* National Formosa University, Taiwan

Protective hard coatings with good mechanical properties and high thermal stability have been widely used in cutting tools and machinery components. Because of the strict conditions in practical applications, multi-component, nanocomposite and multilayered coatings have been developed to replace conventional single-phase, single-layered binary nitrides. Among them, multi-component high-entropy alloy and nitride coatings with a simple solid-solution structure have been intensively studies in recent years and been found to present excellent mechanical properties, thermal stability and wear resistance. In this study, several coatings of Ti-Zr-based quinary high-entropy alloys with the additions of Al, Cr, Mo, Hf, Nb, Ta, and/or V, and their nitrides with various nitrogen contents, were deposited using a multi-target co-sputtering system in an N2/Ar mixed atmosphere. The microstructures, crystal structures and chemical compositions of these coatings were characterized, and the mechanical properties were measured. Because of the effect of high mixing entropies, all the coatings presented an amorphous or a simple face-centered cubic solid-solution structure. The nitrogen contents of the coatings increased with N2/Ar flow ratio. The alloy coatings had a hardness of 6-8 GPa, while the nitride coatings with a low nitrogen content of about 20 at.% easily showed a hardness up to 16-20 GPa. With a high nitrogen content of 50 at.%, very large residual stresses caused the cracking of the coatings and needed to be reduced for preparing more robust and reliable coatings.

BP-ThP-3 $(Ti_{1-x}Y_x)B_{2+\Delta}$ Thin Films - Structural Evolution and Mechanical Properties*, **Martin Truchlý**, B Grancic,* Comenius University in Bratislava, Slovakia*; P Švec Jr.,* Slovak Academy of Sciences, Bratislava, Slovakia*; T Roch, L Satrapinskyy, V Izaii,* Comenius University in Bratislava, Slovakia*; M Harsani,* Staton s.r.o., Slovakia*; O Kohulak, P Kus, M Mikula,* Comenius University in Bratislava, Slovakia

The transition metals boride family offers a lot of stoichiometric modifications (TMB, TMB_2, TMB_6, TMB_{14}, etc.) with different crystalline structure and excellent physical properties. From the point of view of mechanical properties, TM diborides seem to be the most interesting. The best-known overstoichiometric TiB_{2+x} thin film prepared by magnetron sputtering exhibits extremely high hardness H > 40 GPa [1]. However, the application potential of TiB_{2+x} and other binary coatings (ZrB_2, NbB_{2-x}, and W_2B_{5-x}) and the use of their excellent mechanical properties are heavily limited. This is in particular a low fracture toughness expressed by the very high values of Young's modulus (500÷600 GPa) and low oxidation resistance due to formation of volatile boron oxide at 450°C.

Recently, Alling at al. [2] performed extensive theoretical study of 45 ternary diborides with AlB_2 type structure, where the possibility to obtain beneficial age hardening through isostructural clustering, including spinodal decomposition in $M^1_{1-x}M^2_xB_2$ ($M^{1,2}$ = Mg, Al, Sc, Y, Ti, Zr, Hf, V, Nb, Ta) were presented. It has been shown that a significant influence on the formation of a metastable alloy, in which thermally-induced processes led to isostructural clustering, accompanied by age hardening is combination of lattice mismatch between binary constituents and bulk modulus of resulting ternaries.

According to aforementioned results, $(Ti_{1-x}Y_x)B_{2+\Delta}$ seems to be potential candidate for films with clustering tendency what can bring interesting mechanical behavior and extend the possibilities of application potential of diborides.

Here, we present experimental methods and analyzes to investigate structure evolution and mechanical behavior of ternary systems $(Ti_{1-x}Y_x)B_{2+\Delta}$ prepared by magnetron co-sputtering. We discuss the relationship between chemical composition, structural evolution and mechanical properties of as-deposited and annealed thin films based on results obtained from scanning electron microscopy (SEM), X-ray diffraction analysis (XRD), transmission electron microscopy (TEM), and nanoindentation measurements.

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BP-ThP-4 Post-annealing of (Ti,Al,Si)N Coatings deposited by High-Speed Physical Vapor Deposition (HS-PVD)*, K Bobzin, T Brögelmann, C Kalscheuer, T Liang, **Martin Welters**,* Surface Engineering Institute - RWTH Aachen University, Germany

Gas turbine engines operating in environments containing solid particles such as sand, dust and ice particles are challenged by the problem of solid particle erosion (SPE), which causes contour changes especially on compressor blades. Consequently, the performance and efficiency of the engines as well as the maintenance intervals will be reduced. In order to minimize the effects of SPE and to extend the lifetime of compressor blades, the application of erosion resistant coatings represents a promising way.

In the present work, (Ti,Al,Si)N coatings with different Si contents were deposited onto martensitic steel X3CrNiMo13-4 used for compressor blades by High-Speed Physical Vapor Deposition (HS-PVD) technology. Morphology of the coatings investigated by scanning electron microscopy (SEM) shows a dense microstructure with coating thicknesses up to s ≈ 20 µm. Owing to hollow cathode discharge (HCD) and the transport function of the plasma-forming gas Ar, which are specific in HS-PVD deposition processes, high deposition rates ds/dt > 20 µm were achieved. The coated samples were then post-annealed in N_2 atmosphere with bias voltage induced Ar plasma directly in the coating chamber. The annealing temperature, time and atmosphere were varied. The post-annealing effects on the microstructure, indentation hardness as well as chemical and phase compositions were investigated by energy dispersive spectroscopy (EDS), X-ray diffraction (XRD) and nanoindentation, respectively. The erosion resistance of annealed, as-deposited and uncoated samples was investigated using a fine sand blasting facility. Basing on measured erosion rates and inspection of the eroded surfaces, a much higher erosion resistance of the (Ti,Al,Si)N coated samples compared to uncoated substrates could be revealed. Moreover, the post-annealing process led to a further improvement of the erosion resistance. Therefore, the thick (Ti,Al,Si)N coatings deposited by HS-PVD in combination with a post-annealing in N_2 atmosphere provide a high potential for the protection of compressor blades against SPE.

BP-ThP-6 Discrete Thin-film Multilayer Structures of TiB_2 and ZrB_2 Ceramics for Super-hard and Tough Coating*, A Ghimire,* National Tsing Hua University, National Dong Hwa University, Taiwan*; **Ming-Show Wong**,* National Dong Hwa University, Taiwan*; S Chang,* National Tsing Hua University, Taiwan

Multilayer films consisting alternating ZrB_2 and TiB_2 layers with nanometer scale bilayer thickness λ (7nm ~ 1nm) were deposited on silicon substrate by using unbalance magnetron dc sputtering system. The effect of bilayer thickness design on the structure and mechanical properties of the resulting multilayer films has been investigated. The films of bilayer thickness 6 nm and 7 nm possess polycrystalline structure with low crystallinity, however, below 6 nm bilayer thickness, highly [001] textured films with high intensity XRD peaks were witnessed to be lying between ZrB_2 and TiB_2 [001] phase. For 6 nm ~ 2nm bilayer samples, there also exist a unique X-ray diffraction peak along with the alloy phase which is distinct than the conventionally observed superlattice peaks in most of the multilayer works. The hardness increment concurs with the phase transition to aforementioned unique structure. The maximum hardness reached up to 44 GPa for the 2nm bilayer sample with a compressive stress of 4.9 GPa. Over the explored range of λ, all the multilayer films generated shorter cracks than single layer TiB_2 and ZrB_2 films upon Vickers indentation fracture test. Furthermore, the microstructure and growth mechanism of ZrB_2/TiB_2 multilayer system by cross sectional TEM analysis is discussed.

BP-ThP-7 Effect of Bias Voltage on Mechanical Properties of Zr–Si–N Films Fabricated through HiPIMS/RFMS Cosputtering, ***Yung-I Chen**, Y Zheng,* National Taiwan Ocean University, Taiwan*; L Chang,* Ming Chi University of Technology, Taiwan

A previous study has fabricated Zr–Si–N films with Si content of 2–10 at.% through the co-deposition of high-power impulse magnetron sputtering (HiPIMS) and radio-frequency magnetron sputtering (RFMS). The mechanical properties, hardness and Young's modulus, of the HiPIMS/RFMS co-sputtered Zr–Si–N films exhibited linear relationships to their compressive residual stresses. In this work, a negative bias voltage of 50–150 V was applied on the substrates to increase the compressive residual stress of the Zr–Si–N films and the effects on mechanical properties were investigated. The results indicated that the compressive residual stress was increased from −5.0 to −8.8 GPa as increasing the bias voltage from 0 to −150 V; however, the hardness and Young's modulus values exhibited decreasing trends varying from 34.4 to 28.3 GPa and 369 to 299 GPa, respectively, which were accompanied with the decrease in the Si content of the fabricated films from 3.2 to 0.4 at.%.

BP-ThP-11 The Effects of Pulse Frequency on the Growth of Diamond Using Pulse Microwave Plasma CVD, ***Yi Zeng**, Y Sakamoto, T Maruko,* Chiba Institute of Technology, Japan

Diamond has many excellent properties such as high hardness, and high thermal conductivity. Usually diamond is grown on 973-1273 K substrate. However high temperature may cause the film to break or peel off. Pulse oscillation plasma can reduce electron temperature and gas temperature while maintaining electron density. For this purpose, pulse oscillation is used to reduce the synthetic temperature. In this study research of diamond deposition at lower substrate temperature using pulse microwave CVD apparatus and the effect of the pulse frequency on growth rate and quality of the deposit.

Diamond synthesis use pulse microwave CVD. Use Si (100) as the substrate. The pretreatment method is scratched with diamond powder and then clean under ultrasonic environment with acetone. Microwave adopt two modes of continuous oscillation and pulse oscillation. The duty ratio is 50%. The pulse frequency is 250,500,750,1000Hz, respectively. Adjust the microwave output power to control the substrate temperature at 673 K under each condition. The substrate temperature during synthesis is measured by the thermocouple mounted on the bottom of the substrate holder. the flow rate of CH4-CO-H2 is 2-25-200 sccm, and synthesis time is 5 hours. For the synthetic pressure, 5.3kPa is used for pulse oscillation, and 1.3kPa is used for continuous oscillation. Analysis of the surface and section of diamond films are observed by SEM. Qualitative evaluation is carried out by Raman spectroscopy. The plasma state is evaluated by emission spectroscopic analysis by OES.

As a result of SEM observation, the crystal size of diamond by pulse oscillation is larger than continuous oscillation. Although the pressure staying at 5.3kPa, the orientation of the crystal changes from (100) to (111) as the pulse frequency increases. The growth rate of pulse oscillation is 1.5-3 times faster than continuous oscillation. The growth rate is 0.3-0.6μm/h when pulse oscillation is used. Under the condition of this experiment, the growth rate of 500Hz was maximum. In the OES, Hα has the highest emission intensity at 500 Hz. Comparing the Hα emission intensity and the film growth rate, it is recognized that the film growth rate tends to be faster with the condition of high emission intensity. In the Raman spectra, D band (1350 cm^{-1}) and G band (1580 cm^{-1}) are observed under any conditions. On the condition at 500 Hz and 1000 Hz, apparent peak 1000-1200cm^{-1}can be observed. This peak is caused by the miniaturization of diamond crystal. It can be concluded that crystal size is miniaturized by pulse frequency 500Hz and 1000Hz.

BP-ThP-12 Analysis of Reaction Gas States on Synthesis of Boron Doped Diamond by HF-CVD, ***Takuya Maruko**, Y Sakamoto,* Chiba Institute of Technology, Japan

Boron doped diamond (BDD) electrodes are expected to be applied to various applications. The performance of BDD electrodes varies depending on the amount of doped B in diamond. Therefore, it is necessary to synthesize BDD which controlled amount of B in diamond depended on the used applications. In synthesis of BDD, B_2H_6, $B(CH_3)$, $B(OCH_3)_3$ are often used as B dopants, nevertheless there is a disadvantage that B_2H_6 and $B(CH_3)_3$ are toxic. Conversely, $B(OCH_3)_3$ has the advantage of lower toxic relatively. However, it is difficult to control $B(OCH_3)_3$ flow rate, because $B(OCH_3)_3$ is liquid and introduced into the chamber by evaporation or bubbling. Therefore, if it is possible to control the amount of doped B in diamond by in-situ measurement of the reaction gas states, it is considered that more efficient production of BDD electrodes are possible.

In this study, the BDD synthesis was performed by HF-CVD using $B(OCH_3)_3$ as a B source, and analysis of reaction gas states using QMS during synthesis was attempted.

BDD was synthesized by HF-CVD using H_2-CH_4-$B(OCH_3)_3$ as a reaction gas. The $B(OCH_3)_3$ flow rate was varied from 0.1 to 0.4 sccm and CH_4 / H_2 ratio was 2%. The synthesis pressure was 4 kPa, filament temperature was 2273 K. The reaction gas states were measured using QMS. The deposits were evaluated using SEM, XRD, and Raman spectroscopy.

As a result of observation of deposits, facets of diamond crystals were observed under all conditions from surface observation by SEM. The peaks of diamond were recognized in the XRD patterns of the deposits under all conditions. The peaks due to B-doped diamond were recognized in the Raman spectra of the deposits for all synthesis conditions. Therefore, the synthesis of BDD was confirmed under all conditions. Additionally, the position of the peak caused diamond at 1333cm^{-1} in the Raman spectrum was changed lower wavenumber with increasing of the $B(OCH_3)_3$ flow rate. This result suggests that the amount of doped B in the diamond was increased with increasing of the $B(OCH_3)_3$ flow rate.

As a result of measurements of reaction gas states during synthesis by QMS, it was confirmed that peak of OCH_3 molecule was decomposed from $B(OCH_3)_3$. Additionally, the peak height of OCH_3 increased with increase of $B(OCH_3)_3$ flow rate.

In summary, the correlation was confirmed between the peak height of OCH_3 molecules measured from QMS and amount of B in diamond.

BP-ThP-13 Effects of Boronizing Pretreatment on the Adhesion of B-doped Diamond on Ti Substrates, ***Yuuta Izu**,* Chiba institute of Technology, Japan*; T Sakuma,* Ogura Jewel Industry, Japan*; A Suzuki, T Maruko,* Chiba Institute of Technology Graduate School, Japan*; M Imamiya, Y Sakamoto,* Chiba Institute of Technology, Japan

BDD is an ideal electrode material because the potential window is wide, the background current is extremely low and it is insoluble in any solution. Ti / BDD electrodes are promising for application in wastewater treatment, because it has advantages of both materials. However, the delamination occurs at the intermediate layer between BDD coating and Ti substrate. Consequently, it is necessary to design intermediate layer having high bond dissociation energy.

Since the bonding dissociation energy is TiB > TiB_2 > TiC, the introducing Ti-B into the intermediate layer of the BDD on the Ti substrate can be expected to be improved the adhesion strength between the Ti substrate and the BDD film.

The boronizing of each Ti substrate with different reaction time and deposition of BDD on each Ti substrate with different reaction time were conducted using a mode-conversion type microwave plasma chemical vapor deposition apparatus, which is able to consistently process boronizing pretreatment and deposition of BDD, with solution of trimethyl borate as boron source.

From the results of chemical bonding analysis by X-ray photoelectron spectroscopy of the surface of each Ti substrate after the boronizing, it was observed that the amount of synthesizing Ti-B increased with the increase of the boronizing time. In adhesion strength of each BDD / Ti, increasing adhesion strength was accompanied the increase of boronizing time upto 20 minutes. However, adhesion strength at 30 minutes of boronizing time was decreased more than at 20 minutes.

It is considered that the adhesion strength was decreased by progressing hydrogen embrittlement was indicated.

BP-ThP-14 High Entropy Nitride Thin Film ($(Cr_{0.35}Al_{0.25}Nb_{0.12}Si_{0.08}V_{0.20})N_x$) for Tribological Characteristics at High Temperature*, Yu-Chia Lin*, *J Duh,* National Tsing Hua University, Taiwan

High entropy nitride thin films have already been reported because of its outstanding mechanical properties. In this study, adding self-lubricating element Vanadium in high entropy nitride system improved the wear performance due to the formation of Magnéli phase. High entropy nitride thin films $(Cr_{0.35}Al_{0.25}Nb_{0.12}Si_{0.08}V_{0.2})N_x$ with different nitrogen ratio were fabricated by controlling the nitrogen flow ratio in a radio frequency magnetron sputtering system. The variation of nitrogen ratio in thin film will affect the mechanical properties or even the crystal structure, thus investigating the difference of material characteristic induced from different nitrogen ratio become essential.

The chemical composition of as-deposited coatings was detected by a FE-EPMA. The crystal structure was evaluated from a Grazing Incidence XRD. The layer thickness of nitride thin films was measured from SEM. The mechanical properties at ambient temperature and high-temperatures were evaluated by a nano–indenter. The tribological properties were tested by ball-on-disc wear test in a high-temperature tribometer. The results of annealing test in air were also addressed in this study. Finally, a high entropy nitride thin film with the favorable wear performance in high temperature will be briefly discussed. It is expected to be a potential candidate applied in high temperature wearing industry.

BP-ThP-15 Search of New $(Al_{0.25}Cr_{0.3}Nb_{0.1}Si_{0.08}Ti_{0.1}Mo_{0.17})N_x$ Coatings for Feasible Application at High Temperature*, Wei-Li Lo*, *J Duh,* National Tsing Hua University, Taiwan

Recently, mechanical and tribological properties of high entropy alloy(HEA) and HEA nitride coatings have been widely discussed, yet the high-temperature tribology of HEA nitride coatings have not been investigated. In this study, $(Al_{0.25}Cr_{0.3}Nb_{0.1}Si_{0.08}Ti_{0.1}Mo_{0.17})N_x$ coatings with various nitrogen ratios were fabricated on Inconel 718 substrate by RF magnetron sputtering.The chemical composition analysis of $(Al_{0.25}Cr_{0.3}Nb_{0.1}Si_{0.08}Ti_{0.1}Mo_{0.17})N_x$ coating was carried out using a FE-EPMA. The cross-sectional microstructure was observed by a FE-SEM. The phases of the HEA nitride coatings were verified by a Grazing Incidence XRD. The intrinsic mechanical properties of the coatings were measured by a high-temperature nano-indentor. The high-temperature tribological properties were estimated by a ball-on-disc tribometer equipped with a Al_2O_3 ball at high temperature.

$(Al_{0.25}Cr_{0.3}Nb_{0.1}Si_{0.08}Ti_{0.1}Mo_{0.17})N_x$ coating with a specific nitrogen ratio exhibits favorable mechanical properties, which could be attributed to the formation of stable crystalline structure. In addition, the MoO_3 Magnéli phase could be observed at elevated temperature, which also improves the high-temperature tribological properties by providing a lubricating surface. Surface morphology and microstructure of the wear track were observed by FE-SEM and HR-TEM. The elemental redistribution and phase transformations in the wear track were analyzed by XPS and XRD. Finally, a HEA nitride coating with optimal high-temperature mechanical and tribological properties will be investigated and discussed.

BP-ThP-18 e-Poster Presentation: The Role of Vacancies in the W-N System*, F Klimashin,* *Paul Heinz Mayrhofer*, TU Wien, Institute of Materials Science and Technology, Austria

Our experimental and computational investigations afford an insight into the role of vacancies in the structure–properties relationship within the binary system tungsten–nitrogen. The vacancies on metal and nitrogen lattice sites favour the formation of the face-centred cubic structure. The lower the synthesis temperature, the lower the needed nitrogen partial pressure to stabilise the cubic structure. Among cubic γ-$W_{0.50}N$ and γ-$WN_{0.50}$, also compositions with nearly 1:1 stoichiometry were prepared. Our results indicate clustering of vacancies on metal and nitrogen lattice sites rather than single-phased structures of NaCl (mechanically unstable) or NbO (nearly twice as high elastic modulus as experimentally observed) types. All cubic structures show hardness values of 30–33 GPa (up to 37 GPa on austenitic steel) with the tendency to slightly higher values for lower N/W ratios. In contrast, higher N/W ratios tend to increase fracture toughness, as for example 3.4 MPa√m is obtained for γ-$W_{0.5}N$ but only 2.4 MPa√m is obtained for γ-$WN_{0.5}$. Coatings with a 1:1 stoichiometry, where clustered vacancies seem to be present, exhibit 2.8 MPa√m. The fracture toughness clearly scales with the compressive residual stresses, which clearly increase with the N/W ratio.

BP-ThP-19 Probing Defected Layers of MoN/TaN and TiN/WN Superlattices*, Nikola Koutna*, *J Buchinger, R Hahn,* Institute of Materials Science and Technology, TU Wien, Austria*; J Zálešák,* Erich Schmid Institute of Materials Science, Austrian Academy of Sciences, Leoben, Austria*; M Bartosik,* Institute of Materials Science and Technology, TU Wien, Austria*; M Friák, M Šob,* Institute of Physics of Materials, Academy of Sciences of the Czech Republic, Czech Republic*; D Holec,* Montanuniversität Leoben, Austria*; P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Superlattices composed of coherently stacked materials with bi-layer periods in the nm range are an important concept to alter energetic, structural, mechanical, or electronic properties of coatings. Exceptional performance and hardness enhancement beyond the limits of the superlattice building components has been demonstrated for a series of nitride-based superlattices, e.g., TiN/AlN, TiN/CrN, TiN/NbN, TiN/VN, TiN/TaN or AlN/CrN. Yet the fundamental structure-stability-elasticity relationships and their origin remain mostly unknown for superlattices combining even simple binary transition metal nitrides. The complexity of these multilayered systems mainly stems from a strong driving force of transition metal nitrides for vacancies.

Our combined first-principles and experimental study focuses on two cubic-based multilayered systems: MoN/TaN and TiN/WN. MoN, TaN, and WN are often used to improve ductility, but they are metastable (MoN, TaN), or even unstable (WN) in a perfect stoichiometric configuration. Vacancies play an important role for these binaries, since they can largely improve their thermodynamic stability, ensure mechanical stability, or even eliminate (some) soft phonon modes (i.e., contribute to a vibrational stabilisation). By employing Density Functional Theory calculations, we reveal the impact of vacancies on the structural stability as well as on the electronic structure and elastic constants. Theoretical findings are corroborated with X-ray diffraction patterns, energy-dispersive X-ray spectroscopy as well as nanoindentation data. Furthermore, we formulate design rules for MoN/TaN and TiN/WN multilayered coatings with superior elastic properties and/or exceptional tensile strength.

BP-ThP-20 Investigation of CVD Stability Windows for Tungsten Carbide Phases*, Katalin Böör*, *J Gerdin,* Uppsala University, Sweden*; R Qiu,* Chalmers University of Technology, Sweden*; M Boman,* Uppsala University, Sweden*; E Lindahl,* Sandvik Coromant R&D, Sweden

Tungsten carbides are widely used in bulk materials such as cemented carbides, primarily due to their high hardness and chemical resistance. Although there has been extensive research on tungsten carbides, their potential as materials for wear and corrosion resistant coatings has not been widely utilized yet. A few attempts have been made to deposit tungsten carbides with chemical vapor deposition. Typically WF_6, H_2 and a hydrocarbon such as propane were used as precursors. Usually, multiple metallic or carbide phases were obtained such as W, W_3C, W_2C, WC_{1-x} or WC. In addition to the metallic or carbide phases amorphous carbon was also observed to be formed in some cases during the CVD process. Single-phase coatings, however, have only been obtained in a few cases and it has been difficult to control the microstructure and/or morphology of those.

In order to achieve a better control on the characteristics of the coating, a deeper understanding on the influence of the CVD process parameters on the resulted coatings is needed. A systematic study carried out to find the stability window of the single phases in a CVD process will be presented. The study will include the phase content, the microstructure, the morphology of the deposited single-phase tungsten carbide coatings and the growth kinetics behind.

The tungsten carbide thin films were deposited using WF_6, C_2H_4, H_2 as precursors with Ar as the carrier gas on different metallic and ceramic substrates in a newly constructed hot-wall CVD reactor. XRD, GI-XRD, SEM, XPS and TEM- analysis were used to characterize the coatings.

BP-ThP-22 Photocatalytic Activity of Metal Oxide Thin Films Deposited by MS-PVD and Layer-by-Layer for Hydrogen Production by Water Splitting*,* *P Rivero,* Public University of Navarra, Spain*;* ***Jose Antonio Garcia*,** Universidad Publica de Navarra, Spain*; R Rodriguez,* Public University of Navarra, Spain*; J Esparza,* AIN, Ingeniería Avanzada de Superficies, Spain*; G Garcia Fuentes,* Public University of Navarra, Spain

Two different deposition techniques, Magnetron Sputtering Physical Vapour Deposition (MS-PVD) and Layer-by-Layer (LbL) technique, have been utilized to compare the photocatalytic activity of various metal oxides, including single metal oxides: Fe_2O_3, WO_3, binary metal oxides: $SrTiO_3$, and a combination of these compounds. The coatings were deposited on stainless steel (AISI 304) substrates, glass slides and silicon wafers. Photocatalytic activity has been tested by visible spectrophotometry, through monitoring the degradation of Methylene Blue under direct exposure to simulated solar light. Additionally, UV-Vis-NIR spectrophotometry tests have been carried out to measure the changes in the resultant light absorbance of the oxide films. Further characterization has been performed, including Field Emission Scanning Electron Microscopy (FE-SEM), X-Ray Diffraction (XRD), chemical composition profiles by Glow Discharge Optical Emission Spectrometry (GD-OES), corrosion performance by potentiodynamic polarization tests, light interferometry, contact angle measurements and wetting properties. Finally, an exhaustive study of the mechanical properties of the thin films has been carried out.

BP-ThP-23 Nanocomposite (Ti,Al,Cr,Si)N HPPMS Coatings for High Performance Cutting Tools*, K Bobzin, T Brögelmann, N Kruppe, M Carlet,* ***Matthias Thiex,*** RWTH Aachen University, Germany

During the machining of high-speed steels, thermal and mechanical loads occur, which can influence the performance and cause damaging of the cutting tools. Due to their high hardness, wear resistance and toughness, hard coatings are used to improve productivity. The development of a complex coating (Ti,Al,Cr,Si)N for cutting tools and comprehensive analyses of them are the main objectives of the current research. The coating deposition was conducted in an industrial scale coating unit using a hybrid technology, consisting of direct current and high power pulse magnetron sputtering (dcMS/HPPMS). Cemented carbide was used as substrate material. To enhance the cutting performance, a nanocomposite architecture was developed, which consists of crystalline (Ti,Al,Cr)N phases in an amorphous Si_3N_4 matrix. The amorphous matrix aims to reduce the oxygen diffusion into grains and thus, to increase the oxidation resistance. Reduced grain sizes can further improve the mechanical properties such as the resistance of the coating against plastic deformation. The oxide reaction layer formed on the coating's surface upon exposure to the atmosphere has a significant influence on the tool performance. Thus, the design of a diffusion resistant coating system was proceeded by the synthesis of a thin oxynitride toplayer (Ti,Al,Cr,Si)ON, which is not sufficiently studied in the literature. The oxidation behavior of the coated samples under atmospheric conditions and the phase stability under inert gas atmosphere were comprehensively analyzed at high temperatures up to T = 1,300°C. Under both conditions, detailed analysis on diffusion between the workpiece material AISI M2 and the bilayer coatings were additionally performed. By reducing the pulse duration of the HPPMS cathodes, the non-metal to metal ratio was taken into account to study its influence on the reaction layer. Furthermore, the influence of cathode power and bias voltage on the coating properties was investigated. The microstructure was investigated by transmission electron microscopy (TEM). Sputter depth profiles determined using X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) were applied after the heat treatments. Based on the results, the incorporation of oxygen tends to modify the nanocrystalline morphology of the nitride interlayer having grain sizes of d ≈ 10 nm to an amorphous microstructure, which is characteristic for the oxynitride top layer. The coated samples possess high oxidation resistance and diffusion resistivity. Moreover, the coating systems exhibit a significant phase stability.

BP-ThP-26 Low Temperature Titanium Boron-Carbide Based Thin Film Coatings by Plasma Enhanced Chemical Vapor Deposition on Surface Microstructure Controlled WC-Co*,* ***Takeyasu Saito,*** *D Kiyokawa, K Fuji, N Okamoto,* Osaka Prefecture University, Japan*; A Kitajima, K Higuchi,* Osaka University, Japan

Chemical vapor deposited (CVD) or physical vapor deposited (PVD) hard material carting technique is widely used for molds and cutting tools, which plays an important role in a lot of manufacturing industry. For example, titanium carbide (TiC), titanium nitride (TiN) and titanium carbonitride (TiCN) is used in order to increase lifetime or to decrease friction coefficient of molds, tools etc. Recently, titanium borinitride-based hard coating films (TiBCN) have been attracted much attention.

The film prepared by thermal CVD typically carried out around 1000°C has good uniformity and mechanical properties, which restricts substrates having low melting points, and also causes deformation of substrates. Plasma enhanced chemical vapor deposition (PECVD) has some merits like lower deposition temperature (< 500°C) than thermal CVD, however, the films usually have low adhesion strength.

In this study, TiBCN coatings were formed by PECVD with $TiCl_4/CH_4/BBr_3/N_2$ reaction system. Growth rate, surface morphologies, crystallographic properties, and composition ratio/chemical states were evaluated by surface profiler, FE-SEM, XRD, and XPS. Several surface pretreatment methods were investigated to increase surface roughness to enhance adhesion strength, which include, CF_4 plasma etching and aqua regia ($3HCl:HNO_3$) etching.

Figure 1 shows XRD results of TiBC thin films from $TiCl_4/BBr_3/CH_4$ with different CH_4 concentration. Clear TiB_2 peaks were recognized and C(004) peak became recognized when the C/Ti ratio is over 3. Figure 2 shows XRD results of TiBN thin films from $TiCl_4$/ BBr_3/N_2 with different N_2 concentration. TiN(110) increased and TiB_2(101) became weak with increasing N/Ti ratio. Both TiN and TiB_2 peaks exist, suggesting that deposited films contain Ti, B and N when N/Ti ratio =3,5. Based on the results shown in figs. 1 and 2, the deposition properties of TiBCN thin films will be discussed.

BP-ThP-27 Performance of the CrAlSiN and Hydrogen free DLC Combined Hard Coatings Deposited on Micro Tools Cutting Printed Circuit Board*, D Wang,* MingDao University, Taiwan*;* ***Li-Chi Hsu,*** *J Hung,* Aurora Scientific Corp., Canada*; W Chen, W Ho,* MingDao University, Taiwan

Coating systems, including CrAlSiN coatings and various CrAlSiN +DLC combined coatings were deposited using a cathodic arc evaporation system. All the coatings were finished by using technology of modified pulsed current output to the arc evaporators. The DLC coatings were obtained with graphitic target and various mixture of N_2+ Ar gases. All the coating systems with the effects of various conditions on the properties and performance in field of machining printed circuit boards were studied. The properties of the CrAlSiN coating was used as a reference coating. The various CrAlSiN+DLC coatings were evaluated using ball-on-disc wear tests. The wear behavior of the CrAlSiN+DLC combined coatings was affected by the various mixture of N_2+ Ar gases. The hardness of the CrAlSiN+DLC combined coatings increase up to 40GPa as compared to CrAlSiN coating of 35GPa. Furthermore, the cutting performance of micro tools with the various coatings were evaluated by cutting the PCB board. Micro tool with CrAlSiN coatings increased the significant amount of cutting distance as compared to the blank tool. Meanwhile, the tools deposited with CrAlSiN+DLC combined coatings showed the maximum cutting distance of the PCB board which helped to improve tool wear and cutting performance.

Keywords: Pulsed current, cathodic arc evaporation, CrAlSiN, DLC

BP-ThP-28 Study and Characterization of the Vanadium Carbide Interlayer Deposited by Laser Cladding over Carbon Steel for CVD Diamond Growth*, D Damm, R Pinheiro, J Gomez,* National Institute for Space Research (INPE), Brazil*; A Contin,* Federal University of Goiás (UFG), Brazil*; R Correia,* Federal University of São Paulo (UNIFESP), Brazil*; R Volu,* Institute for Advanced Studies (IEAV), Brazil*;* ***Vladimir Jesus Trava-Airoldi,*** National Institute for Space Research (INPE), Brazil*; G de Vasconselos,* Institute for Advanced Studies (IEAV), Brazil*; D Barquete,* Santa Cruz State University (UESC), Brazil*; E Corat,* National Institute for Space Research (INPE), Brazil

Vanadium carbide has been used in the industry to improve the steel properties. It was extensively studied and explored by Toyota a few decades ago. Vanadium has high hardness, as well as carbides forming ability, chemical compatibility with carbon steel and CVD diamond and an intermediate thermal expansion coefficient (TEC) between these materials. These characteristics make vanadium carbide attractive as an intermediate layer for CVD diamond applications. There are many techniques to obtain a vanadium carbide interface such as thermodiffusion and sputtering. In this work, we will discuss the vanadium carbide deposition by laser cladding on carbon steel surface. The main problems in growing CVD diamond directly on steel surface are related crystallinity, purity and adhesion. The crystallinity issue is due to the fact that the gas phase carbon goes in to the steel substrate bulk causing its embrittlement and reducing diamond growth rate. The problem regarding purity is related to the transitions metals present in the steel surface (such as iron and cobalt) that inhibit the sp3 bond over the sp2 bond, providing the appearance of graphite on CVD film that reduces the film quality. As for the Adhesion challenge, the TEC mismatch results in a high residual compressive tension in the diamond film, which causes delamination during cooling. Therefore, an intermediate layer is necessary to create a transition zone able to relieve the thermal residual stress and also to act as a diffusional barrier. The laser cladding was selected because of its rapid processing, excellent metals adhesion by melting, good surface finish reducing roughness and capacity to preserve the original properties of the material substrate interacting only with the up layers of the material. In this study, we analyze vanadium carbide phase formation by varying systematically the following parameters: resolution (300 – 900 DPI); scanning speed (100 – 500 mm/s); and output power (40 –

125 W). For the substrate we used AISI D6, AISI O1 and AISI M2 steels. The HFCVD films were grown using the following parameters: 2 sscm of CH_4; 98sccm of H_2; 2h deposition process time; 700°C and 5mm of work distance. The results of LCVC coating and HFCVD films characterizations were obtained by X-ray diffraction, scanning electron microscope field emission (SEM-FEG) and Raman spectroscopy.

BP-ThP-30 Optimization for Adhesion Properties of c-BN Films Coated with HiPIMS*, Ihsan Efeoğlu, Y Totik, A Keleş,* Ataturk University, Turkey

Friction and wear are one of the most important problems for machine components working in contact with each other. In order to reduce friction and wear, films with desired properties are usually coated on the surface of component. One of the most phenomena of these coatings is c-BN films. Although c-BN films have superior properties, their low adhesion property needs to be improved. Therefore, in this study, optimum adhesion properties were investigated for c-BN film coated with HiPIMS. Taguchi L9 orthogonal array test setup was used to determine the optimum adhesion. The scratch tester was conducted to define adhesion property. Three different parameters (N_2 content, duty cycle and B_4C target voltage) and three different levels for each parameter have been selected in Taguchi. The results obtained from the experiments were converted to signal/noise rate (S/N) and used to optimize the adhesion value of c-BN films. These values are in order of N_2 content, duty cycle and B_4C target voltage 3.5 sccm, 4.5% and 900V, respectively. Verification coating and test were performed for the optimum values obtained.

BP-ThP-31 Si-DLC Films Prepared by Magnetron Sputtering under Different Working Pressure*, Chaoqian Guo, S Lin, Q Shi, C Wei, H Li, W Wang, M Dai,* Guangdong Institute of New Materials, China

Si-DLC films were prepared on cemented carbides by high power impulse magnetron sputtering combined with middle-frequency magnetron sputtering. A graphite target providing carbon source was driven by high power impulse magnetron sputtering while silicon was originated from two SiC targets powered by middle-frequency magnetron sputtering. Mechanical and tribological properties of Si-DLC films deposited under different working pressure were studied. Scanning electron microscope, Raman spectroscopy and X-ray photoelectron spectroscopy were applied to investigate film microstructure and bonding states of elements. Nanoindentation, scratch tester and tribometer were used to test films' mechanical and tribological properties. The results showed that working pressure affects Si-DLC films' structure and properties greatly.

BP-ThP-32 Multielement Rutile-structured AlCrNbTaTi-oxide Coatings Synthesised by Reactive Magnetron Sputtering*, Alexander Kirnbauer, C Koller,* TU Wien, Institute of Materials Science and Technology, Austria*; S Koloszvári,* Plansee Composite Materials GmbH, Germany*; P Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

A new alloying concept gained tremendous attraction in the field of materials research within the last years—so-called high-entropy alloys. These are defined as alloys with a configurational entropy of at least 1.5 R (R being the universal gas constant). To reach this specific value, the alloy ought to consist of at least 5 elements in a compositional range between 10 and 30 at.%. This concept may also be transferred to ceramic-based materials, in which the respective constituents are binary ceramics borides, carbides, nitrides ,or oxides—the latter of which are subject to the present study.

AlCrNbTaTi-oxide coatings were prepared by reactive magnetron sputtering in a lab-scaled deposition system using a single powder-metallurgically produced compound target (composition AlCrNbTaTi 20/20/20/20/20 at.%). Systematic variations of the O_2/Ar-ratio used for the deposition of these high-entropy films to determine basic structure-property–relationships.

The coatings crystallise partly in a single-phased rutile structure, are slightly enriched in Ta and exhibit nearly a MeO_2 stoichiometry with an oxygen content of ~64 at.%. The indentation hardness of ~20 GPa in the as-deposited state is for some of the coatings slightly higher than compared to binary or ternary oxides. The thermal stability was investigated by vaccum annealing treatments with subsequent XRD and indentation measurements to gain information about the evolution of the structure and the mechanical properties.

Our results clearly show that a high-entropy concept applied to oxide thin films using a single powder-metallurgically-produced compound target is a promising strategy in promoting single-phased and mechanically/thermally- stable AlCrNbTaTi oxide coatings.

BP-ThP-33 Magnetron Sputtering of Tungsten-containing /TiNxOy Multilayered Solar Selective Coatings*, Siang-Yun Li, Y Shen, K Chang, J Ting,* National Cheng Kung University, Taiwan

In this study, we prepared multilayer coatings of tungsten-containing TiNxOy having different compositions for use as solar selective absorbers. First, we sputtered a tungsten reflective layer on stainless steel substrate and W/TiNxOy layers havng two different compositions as the solar absorption layers. Finally, we sputtered HfO_2 as the outermost reflective layer. We adjusted the N/O ratio and film thickness to optimize the performance of TiN_xO_y multilayered solar selective coatings. The coatings were characterized using before and after 600-800 C heat treatment. Effects of the materials characteristics on the optical properties were discussed.

BP-ThP-34 Electron-configuration Stabilized (W,Al)B_2 Solid Solutions*, R Hahn, Vincent Moraes, P Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria*; A Limbeck,* Institute of Chemical Technologies and Analytics, TU Wien, Austria*; P Polcik,* Plansee Composite Materials GmbH, Germany*; H Euchner,* Helmholtz Institute for Electrochemical Energy Storage, Germany

Recent investigations on boride based materials, pointed out, that WB_{2-z} - in its metastable α-structure (AlB_2-prototype) - draws an interesting base system for the development of ternary material systems with exceptional performances in the field of hard and tough coatings.

In this study, we present a combined experimental and theoretical study of the ternary diboride system $W_{1-x}Al_xB_{2-z}$. Tungsten rich solid solutions of $W_{1-x}Al_xB_{2-z}$ were prepared by physical vapor deposition and investigated for structure, mechanical properties and thermal stability. All crystalline films show hardness values above 35 GPa, while the highest thermal stability was found for low Al contents. In this context, the impact of point defects on the stabilization of the AlB_2 structure type is discussed, using ab initio methods. Most notably, we are able to show that vacancies on the boron sublattice are detrimental for the formation of Al-rich $W_{1-x}Al_xB_{2-z}$, thus providing an explanation why only tungsten rich phases are crystalline.

Keywords: $W_{1-x}Al_xB_{2-z}$, sputtering, vacancies, density functional theory

BP-ThP-35 Apparent Fracture Toughness of TiN Coatings with Alternating Stress Fields*, Antonia Wagner, J Buchinger,* TU Wien, Institute of Materials Science and Technology, Austria*; M Todt,* TU Wien, Institute of Lightweight Design and Structural Biomechanics, Austria*; D Holec,* Montanuniversität Leoben, Austria*; P Mayrhofer, M Bartosik,* TU Wien, Institute of Materials Science and Technology, Austria

In general, ceramic thin films show a low fracture toughness and tend to catastrophic brittle failure. One of the most important approaches to increase the crack growth resistance of ceramic components is to introduce compressive residual stresses. When considering coatings manufactured by physical vapor deposition the intrinsic residual stresses can be modified by applying a negative bias voltage to the substrate and hence altering the degree of ion bombardment. Depositing a chemically homogeneous material with a sequential variation of the bias voltage leads to a multilayer coating in the sense of residual stresses, whereas the material properties are kept more or less constant over the film thickness . This approach allows studying the effect of residual stresses on the fracture behavior of multilayers decoupled from other mechanisms like elastic mismatch.

Herein, TiN coatings are deposited on Si (100) substrates by reactive magnetron sputtering and different multilayer architectures with respect to the residual stress state are realized by changing between a bias voltage of -30V and -60V. The curvature of the substrate is measured and an analytical model based on Euler-Bernoulli-beam theory is applied to investigate the stress distribution within the coating. Fracture experiments are performed on micro cantilevers fabricated by focused ion beam milling which eventually are compared with fracture toughness estimations based on the calculated stress distributions.

BP-ThP-36 Synthesis and Structural Characterization of Nanostructured $CN_{0.1}$ Films Deposited by RF Magnetron Sputtering at Different Bias Voltajes*, Arturo Lousa, D Cano, C Villabos, J Esteve,* University of Barcelona, Spain

Nitrogen content of about 10% can be considered as the border between nitrogen doped amorphous carbon (DLC:N) and fullerene-like carbon nitride (CN_x) thin films. In this sense, this material can be a good alternative to reduce the high values of stress usually found in pure DLC coatings while keeping most of its good mechanical, tribological and biocompatible properties.

The present investigation is centered on the deposition of relatively thick films (0.5 mm) of $CN_{0.1}$with N concentration of around 10% by RF magnetron sputtering. Samples were deposited at negative bias voltage between –20 and –150 V in order to study the effect of different intensities of ion bombardment during the film growth on the film structure. Monocrystalline Silicon wafers were used as substrates for all the deposited samples, and CoCrMo substrates were occasionally used in order to test the applicability on biomedical components. These films were characterized by X-ray photoelectron spectroscopy, (XPS) Raman spectroscopy, FTIR scanning and transmission electron microscopy (HRTEM). Hardness an elastic modulus were measured by the nanoindentation technique.

The deposition rate was 0,5 mm/h. Films showed a columnar structure with atomic composition of 10% N and 90 % C, with a relative composition of sp^3 C-C bonds which decreased slightly as the negative bias voltage was increased. The Raman spectra were deconvoluted in four Gaussians showing more complex contributions than the two conventional G and D. The FTIR results corresponds to electrical conductive samples, with an absorption band corresponding to four different vibration modes of the C-N bonds. The HRTEM diffraction patterns of selected area reveal an essentially amorphous condition. However, as the bias is smaller, some ordering is observed oriented parallel to the substrate. The images of bright field show a homogeneous aspect with a coherent interface and a uniform thickness, with a presence of a distribution of nanometric clusters in an amorphous matrix, denser and with smaller cluster size as the negative bias voltage decreases. Hardness values are in the range of 21–24 GPa, and the modulus of elasticity are in the range of 140–180 GPa with a slight tendency to increase as the negative bias voltage is increased.

BP-ThP-37 An X-ray Diffraction Study on CrAlN and CrAlSiN PVD Coatings*,* ***Jan Latarius****, D Stangier, C Albers, K Berger, M Elbers, A Sparenberg, G Surmeier, M Paulus, C Sternemann, W Tillmann, M Tolan,* TU Dortmund University, Germany

As the demand for highly resistant tools for milling and drilling applications is rising, this translates to more sophisticated coatings, to cope with special requirements as high temperature or corrosion resistance. Very promising candidates are coatings produced by physical vapor deposition (PVD).

Here, CrAlN based PVD coatings have proven to be quite capable to match the claims and CrAlSiN as a possible successor might feature improvement in many critical aspects like hardness, wear resistance, thermal and mechanical stability. These macroscopic properties are reflected in microscopic structural properties and can therefore be studied through means of X-ray diffraction (XRD) by determination of phase composition, residual stresses, micro strains and crystallite size, etcetera.

We present an XRD study on different CrAlN and CrAlSiN PVD coatings. These coatings were produced with varied bias potentials and tempered under air at temperatures between room temperature and 1000° C. The coatings were investigated at beamline BL9 at the synchrotron light source DELTA (Dortmund, Germany). The phase composition, micro strain and crystallite size were determined. The CrAlSiN coatings show a much higher oxidation temperature indicating great benefits of doping with silicon.

BP-ThP-41 Influence of Oxygen Addition on Microstructure and Properties of TiAlN*,* ***Damian Mauritius Holzapfel****, M Hans,* RWTH Aachen University, Germany*; A Eriksson, M Arndt,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; D Primetzhofer,* Uppsala University, Sweden*; J Schneider,* RWTH Aachen University, Germany

Industrial cutting and forming processes have high demands regarding chemical and mechanical properties of coatings, to serve as effective wear protection. Coatings in the TiAlN-system are widely used in industry. In this study TiAlN and $(TiAl)_z(O_xN_{1-x})_{1-z}$ thin films were deposited by cathodic arc evaporation onto cemented carbide substrates. Structure and composition were investigated by X-ray diffraction, scanning transmission electron microscopy, elastic recoil detection analysis and atom probe tomography. The effect on microstructure and properties as influenced by O were characterized.

BP-ThP-42 An Investigation on Synthesis of Novel Oxide-Based Superhard Cr-Zr-O Coatings*, M Mohammadtaheri, Q Yang, Y Li,* ***Jesus Corona-Gomez****,* University of Saskatchewan, Canada

Synthesis of ternary Cr-Zr-O coatings was performed on silicon wafers and glass substrates by Reactive dual radio-frequency (RF) magnetron sputtering technique. The zirconium concentration of coatings changed in a range of 0-10 at. % by tuning the RF power of Zr target. The correlation between the chemical composition, crystal structure, phase composition, and hardness of coatings was investigated by Energy Dispersive Spectroscopy (EDS), X-ray diffraction (XRD), Raman spectroscopy, and Nanoindentation, respectively. Annealing procedures were conducted for 3 hours at 300, 700, 800, and 1000 °C to evaluate the structural stability of the Cr-Zr-O coatings. The results indicated that incorporation of zirconium increases the crystallization temperature of coatings and the excess of zirconium transferred the coatings to a completely amorphous structure. The superhardness (Hardness ≥ 40 GPa) in Cr-Zr-O system was achieved in a specific chemical composition where the Zr content was about 2 at. %. According to the XRD results obtained after annealing treatments, it was confirmed that the zirconium was in a super-saturated solid solution state in the chromium oxide crystal structure where the superhardness was achieved. However, the thermal stability of Cr-Zr-O coatings was higher than pure chromium oxide coatings, their structure was not stable at a temperature higher than 700 °C and their high hardness dropped to 30 GPa after 3 hours annealing at 800 °C. A heat treatment at 1000 °C is required to completely segregate Zr from the chromium oxide crystal structure to create a ZrO_2-Cr_2O_3 composite microstructure in the superhard coatings.

BP-ThP-43 Study of Erosion on Metals and Ceramic Coated Metals Using Magnetron Sputtering Process*, S Hill, D Mihut, A Afshar, Z Grantham, S Sanchez-Lara,* ***Christopher D. Raffield****, N Cordista, S Sanchez Lara,* Mercer University, USA

Solid particle impact erosion is a progressive loss of the materials' mass that results from repeated impact of the erodent particles on the material surface. Materials selection for equipment components working in this type of aggressive environmental condition is a great challenge. These materials must possess high strength, hardness, toughness, corrosion resistance but also high erosion resistance. This study uses an impact erosion tester to observe the effects of accelerated erosion on aluminum 6061 alloy and 4140 heat treated steel and assess their erosion behavior improvement after coating with titanium nitride and chromium nitride ceramics. A two phase mixture of water/sand is circulated in a custom test fixture and allowed to impact test coupons at specified angles. The set of experiments uses multiple sand concentrations, a fixed liquid flow rate, and a constant impact angle during the testing procedure to determine the improvement of erosion with the thin film coating. The ceramic thin film coatings on the samples are deposited using magnetron sputtering equipment, the thickness of the coatings is measured using a profilometer and the compositional structures of the coatings are characterized using X-Ray diffraction. The coating morphology and thin films adherence was investigated using Scanning Electron Microscopy (SEM).

Hard Coatings and Vapor Deposition Technologies
Room Golden West - Session B2-2-FrM

CVD Coatings and Technologies II

Moderators: Kazunori Koga, Kyushu University, Japan, **Francis Maury**, CNRS-CIRIMAT

9:20am **B2-2-FrM-5 Scale up of the DLI-MOCVD Process to Treat 16 Nuclear Fuel Cladding Segments in Parallel with a Protective CrC_x Coating***, A Michau, F Addou,* CEA, Université Paris-Saclay, France*; Y Gazal, F Maury, **Thomas Duguet**,* CIRIMAT, France*; R Boichot, M Pons,* Université Grenoble Alpes, CNRS, France*; E Monsifrot,* Dephis, France*; F Schuster,* CEA, PTCMP, France

Direct liquid injection – metalorganic chemical vapor deposition (DLI-MOCVD) is the most advanced process dedicated to the internal protection of nuclear fuel cladding in accident conditions such as loss of coolant. A coating composed of amorphous chromium carbide CrC_x can be grown by DLI-MOCVD. It is resistant against high-temperature oxidation in air and steam. A joint development between experimental and numerical studies has led to a coating of uniform thickness inside the cladding. Optimized reactor parameters consist in a combination of low temperature (~ 600 K) and low pressure (~ 600 Pa) with a high vapor flow rate ensuring a short residence time of reactive species in the reactor.

Interestingly, CrC_x coatings deposited from the decomposition of a bis(arene)chromium(0) precursor at low temperatures, around 600 K, exhibit the same characteristics than the coatings grown at higher temperatures (623, 648, 673 and 723 K). A similar glassy-like and dense microstructure is achieved; specific to the amorphous nature of the material. No significant differences are detected in TEM, XRD, EPMA and Raman spectroscopy, regardless of the substrate (silicon wafers, 304L and zirconium alloy coupons). It indicates a strong flexibility of the DLI-MOCVD process when combined with an adequate selection of metalorganic precursor.

Since the above-mentioned materials characterizations demonstrate that low temperature coatings possess the appropriate protection properties, the low-temperature DLI-MOCVD process can be scaled-up. The final geometry to be coated is the internal surface of 4 m-long tubes with a diameter < 1 cm. Several runs are successfully achieved with a single segment, 3 segments in parallel, and finally a batch of 16 segments. 3D computational simulations of the deposition process validate the design of the gas-phase distributor flanges (for 3 and 16 segments) which are required to split homogeneously the reactive gas flow towards each segment. Experimental conditions have been extrapolated from 1 to 3 and to 16 cladding segments, resulting in the deposition of the CrC_x coating inside all segments with a uniform partition. Indeed, the total mass intakes over deposition time (g/min) are similar in all 3 or 16 segments.

Overall, this paper demonstrates the feasibility of the deposition of CrC_x coating in a bundle of several, up to 16, nuclear fuel cladding segments of 1 m in length, in order to protect them during accident conditions. This “batch demonstration” is a first step in the course of industrialization. Next step will be the deposition in a full-length cladding (4 m).

9:40am **B2-2-FrM-6 Assessment of Low Temperature CVD Routes to MAX Phases in the Cr-Si-C System***, A Michau,* CEA, Université Paris-Saclay, France*; **Francis Maury**,* CIRIMAT, France*; F Schuster,* CEA Cross-Cutting Program on Materials and Processes Skills, France*; T Duguet,* CIRIMAT, France*; E Monsifrot,* Dephis, France

Different CVD routes have explored for the growth of mixed carbide coatings in the system Cr-Si-C, especially the MAX phases of this ternary system. The goal was to find suitable precursors and typical growth conditions, which could be further optimized to develop an advanced process for industrial applications. For this objective, DLI-MOCVD is an emerging CVD process that combines the use of metalorganic precursors (MO) and direct liquid injection (DLI) of the reactive sources. The main advantages are a significant reduction of deposition temperatures (required for sensitive substrates and energy saving) and the production of high vapor flow rates to feed large-scale reactor.

The solid compound $Cr[CH_2Si(CH_3)_3]_4$, has been used as single-source precursor by DLI-MOCVD in a hot-wall reactor. A solution in toluene (2.9 $\times 10^{-2}$ mol.l^{-1}) was injected in a flash vaporization chamber directly connected to the reactor containing the substrates. The coatings were obtained under low pressure (6.7 kPa) in the temperature range 613-733 K. They are XRD amorphous and exhibit a smooth surface morphology with a dense and homogenous microstructure. Growth rates in the range 0.5-1 µm/h were obtained but the films were partially oxidized due to the high sensitivity of this single-source precursor to oxygen. The Si:Cr atomic ratio of coatings is about 1.1 which significantly lower than the amount bring by the precursor (4). This atomic ratio is relatively close to the value 0.6 of a previously reported ternary phase ($Cr_5Si_3C_2$) but far from the MAX phases Cr_2SiC (0.5) and Cr_3SiC_2 (0.33). Finally this route did not allow to control the Si:Cr atomic ratio in a sufficiently wide range, especially that of MAX phases.

To gain flexibility in the DLI-MOCVD process, a simple one-pot dual-source process has been investigated in a similar reactor. In this 2nd route, bis(ethylbenzene)chromium(0), $Cr(C_6H_5C_2H_5)_2$, and diphenylsilane, $(C_6H_5)_2SiH_2$, were used as liquid molecular precursor of Cr and Si, respectively. A solution containing both precursors in toluene with various mole ratios was used to produce the reactive gas phase via a single pulsed injector. Depositions were carried out under low pressure (6.7 kPa) in the temperature range 723-773 K on various substrates. $Cr_xSi_yC_z$ coatings have been obtained with growth rates as high as 5 µm.h^{-1} and compositions depending mainly on the composition of the injected solution. The coatings were characterized by many techniques (SEM, XRD, TEM, EPMA…) and preliminary properties including thermal stability and oxidation resistance have been investigated. It is demonstrated that DLI-MOCVD process is a promising route to deposit MAX phases.

10:00am **B2-2-FrM-7 Towards CVD of Hard Coatings Using Hetero-Metallic Precursors***, **Sebastian Öhman**, M Ek,* Uppsala University, Angstrom Laboratory, Sweden*; R Brenning,* Sandvik Coromant R&D, Sweden*; M Boman,* Uppsala University, Angstrom Laboratory, Sweden

CVD of hard coatings used for machining and cutting is a field in fast development. However, progress in this area is impeded by the lack of adequate control for nucleation and film growth, which governs the desired mechanical and physical properties of these films. In addition, today's wear resistant coatings are commonly based on single phased binary material systems, yet the increasing demands put on tomorrow’s coatings will require the development of new, multicomponent and multifunctional coatings. Such coatings can be made by combining conventional CVD with the development of new hetero-metallic precursors. This opens for new chemical pathways, better stoichiometric control, higher yields, more versatility and simplified CVD processing.

In this session, a presentation will be made regarding the use of hetero-metallic precursors for CVD. Audience will also be introduced to a newly developed 3-zone hot-wall reactor that enables the flexible deposition from such precursors, in particular those based on titanium and aluminium alkoxides. With the current experimental set-up, it is possible to use several hetero-metallic precursors at once or sequentially (i.e. pulsed CVD).

The synthesised CVD films were characterised using several methods, including XRD, SEM/EDS, TEM, Raman and RBS.

10:20am **B2-2-FrM-8 CVD of Tungsten, Tungsten Nitride and Tungsten Carbide Multilayers***, J Hulkko, K Böör,* Uppsala University, Angstrom Laboratory, Sweden*; R Qiu,* Chalmers University of Technology, Sweden*; E Lindahl,* Sandvik Coromant R&D, Sweden*; **Mats Boman**,* Uppsala University, Angstrom Laboratory, Sweden

Tungsten-based CVD has been investigated since the early 1960. Today, tungsten-based coatings can be found in many technological areas, ranging from electrical contacts and diffusion barriers to wear- and corrosion resistant films as well as absorber coatings in solar cells.

The aim in this study was to create new multi-layered coatings of W/WN, W/WC and WN/WC by varying the thickness and phase composition of the layers.

W/WC/WN thin films were deposited from a reaction gas mixture containing WF_6 and H_2 using Ar as carrier gas. NH_3 and C_2H_4 were added during the nitride- and carbide formation steps. The films were deposited on n-type Si(111)- and Al_2O_3(0001)-substrates, in a newly constructed CVD-equipment built in-house. This equipment is characterised by excellent repeatability using a custom software controller and a wide parameter space to work within, for instance partial pressures and temperature.

The coatings were characterised using several XRD techniques. SEM images provide microstructural information and thickness. Additionally XPS and TEM were used to gain more in-depth chemical and structural information. Vickers nano-indentation was used for hardness investigation.

10:40am **B2-2-FrM-9 Deposition of Carbon Nanoparticles Using Multi-Hollow Discharge Plasma CVD for Synthesis of Carbon Nanoparticle Composite Films**, ***Kazunori Koga***, *S Hwang,* Kyushu University, Japan*; T Nakatani,* Okayama University of Science, Japan*; J Oh,* Osaka City University, Japan*; K Kamataki, N Itagaki, M Shiratani,* Kyushu University, Japan

Carbon Coating films are receiving much attention as an alternative to improve the physical and chemical characteristics of material surfaces. Meanwhile, as the application field diversifies, there have been increasing requests for an improvement in optoelectronic, physical, and chemical properties of the films. Nanoparticle composite films are very promising, since they are expected to improve the film performance [1]. To further understand the films, nanoparticle synthesis and their deposition are important. In this study, gas flow and bias voltage effects on their deposition were studied, using a multi-hollow discharge plasma CVD (MHDPCVD) method. The experiment was carried out in room temperature with CH_4+Ar MHDPCVD, which can continuously produce nanoparticles [2]. Carbon nanoparticles were synthesized at 8 hollows of 5 mm in diameter where Ar and CH_4 pass through. They were transported to the substrate set 50 mm away from the multi-hollow electrode and then deposited. During the process, 60 MHz rf power of 40 W was applied and working pressure and gas ratio of Ar and CH4 were kept at 2 Torr and 6:1 respectively. Also, carbon nanoparticles that were deposited under the control of total gas flow rate from 10 sccm to 200 sccm were analyzed through a transmission electron microscope (TEM). The average size gradually decreased from about 250 nm at 10 sccm to 31.7nm at 120 sccm and the area density increased, but nanoparticles were not detected at conditions over 125 sccm . When the substrate was biased at +50V DC, the nanoparticles of 24 nm in average size were deposited at 125 sccm, becase negatively charged nanoparticles were attracted to the positively biased substrate. Hence, the gas flow rate and the bias voltage are the keys to control of nanoparticles for carbon nanoparticle composite films.

[1] Peter Greil, Advanced engineering materials / volume 17, issue 2, 2014.

[2] K. Koga, et al., Thin Solid Films 506 (2006) 656.

11:00am **B2-2-FrM-10 Hot Filament CVD Diamond Coating Technology for Cutting Tool Applications**, ***Michael Woda***, *W Puetz, M Frank, C Schiffers, W Koelker, O Lemmer, T Leyendecker,* CemeCon AG, Germany

Besides a variety of DLC based coatings for tribological applications, pure diamond (100% sp3 bonded, crystalline carbon) is a very useful coating material system in the group of carbon based coatings for cutting of hard to machine materials. Nowadays Diamond coatings are typically applied to cutting tools with complex geometries by means of Hot Filament CVD thin film deposition. The technology is well established on an industrial scale. The basic principle of this Hot filament CVD diamond deposition technology and the details on the corresponding coating equipment are presented here. Results of case studies dealing with cutting applications on machining of various examples of highly abrasive materials with pure CVD Diamond thin films are discussed in this work. These case studies include applications with Carbon Fiber Reinforced Plastics (CFRP) systems for aerospace industry, ceramic materials as zirconium oxides for dental applications up to direct milling of sintered cemented carbide.

Hard Coatings and Vapor Deposition Technologies
Room California - Session B5-2-FrM

Hard and Multifunctional Nanostructured Coatings II

Moderators: Tomas Kozak, University of West Bohemia, **Helmut Riedl**, TU Wien, Institute of Materials Science and Technology

9:00am **B5-2-FrM-4 Microstructural and Mechanical Stability of TaCu Composite Coatings**, *A Bahrami, C Onofre, A Delgado,* Universidad Nacional Autonoma de México, México*; T Huminiuc, T Polcar,* University of Southampton, UK*; **Sandra Rodil**,* Universidad Nacional Autonoma de México, México

In this study, binary Cu-Ta alloys with Ta content between 0 and 100 % were prepared by co-magnetron sputtering. The effect of elevated temperature vacuum annealing on the morphological stability and mechanical properties of Cu–Ta films was studied. Their structural and mechanical properties were characterized by X-ray photoelectron spectroscopy (XPS), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM) and nanoindentation methods. The XRD results show that a Ta-rich CuTa amorphous phase is formed in the coatings with 15-67 at. % Ta along with nanocrystalline Cu. TEM analyses of two selected samples with 25 and 67 at. % Ta depict formation of crystalline Cu islands in an amorphous CuTa matrix in both as-deposited and annealed coatings. XPS profiles show that the coatings are mainly metallic, with a thin oxide layer. Moreover, analysis of the oxide layer, indicated that Cu nanocrystals are protected against oxidation by the Ta-rich CuTa amorphous layer. A significant increase in hardness values from 0.9 for pure annealed Cu to 11.89 GPa for the samples with 98 at. % Ta, is observed. Also, it was observed that the coatings preserve their microstructural and mechanical stability after vacuum annealing at 550 °C.

9:40am **B5-2-FrM-6 Tantalum Alloying - Improvement of Thermal Stability and Mechanical Properties of Ternary and Quaternary Transition Metal Nitrides**, ***Branislav Grancic***, Comenius University in Bratislava, Slovakia*; D Sangiovanni,* Linköping University, Sweden, Ruhr-Universität Bochum, Germany*; T Roch, M Truchlý, M Mikula,* Comenius University in Bratislava, Slovakia **INVITED**

Combining the high hot-hardness to enhanced toughness and good oxidation resistance is one of the greatest challenges in material-design of transition metal nitride (TMN) ceramics, which are widely employed as protective coatings in machining industry.

In Ti-Al-N and Cr-Al-N, well-known Al-containing TMNs, the thermally-induced decomposition of the cubic solid solution via spinodal mechanism or precipitation leads to the formation of fine-grained nanostructures and the associated age hardening. However, continuous thermal load/unload cycling during industrial machining cause transformation into thermodynamically more stable coarse-grained structures containing hexagonal AlN and cubic TiN or hexagonal CrN_x phases resulting in degradation of mechanical properties. In addition, brittleness limits the use of TMN-AlN alloys in applications demanding a high fracture-resistance.

The concept of multicomponent alloying with elements from groups IIIB – VIB (Y, Zr, Hf V, Nb, Ta, Mo, and W) represents a suitable way to improve the properties of Al-containing TMNs. From this group, pentavalent tantalum is a very attractive substitutional element which is used, for example, in Ti-Al superalloys to improve ductility, and to reduce oxidation at high temperatures. Moreover, the Ta-N phase diagram exhibits a large variety of Ta_yN_x structures, characterized by different electronic properties.

Here, the role of tantalum as a substitution atom improving thermal stability and mechanical properties is presented in several ternary and quaternary systems. In the first case, we combine experiments and *ab initio* calculations to investigate thermally induced age hardening in tough Ta-Al-N coatings via spinodal decomposition. The increase in hardness from 29 GPa to 35 GPa was observed during early stages of phases separations when temperature exceeded 1000°C. In the next case, a significant improvement in toughness of nitride coatings was observed in highly TaN-alloyed Ti-Al-N. While the hardness of $Ti_{0.46}Al_{0.54}N$ (32.5 GPa) is not significantly affected by alloying with TaN, the elastic stiffness monotonically decreases from 442 to 354 GPa with increasing Ta contents indicating enhanced toughness in TiAlTaN. In the last presented Cr-Al-Ta-Y-N system, the presence of Ta in the solid solution shifts the decomposition process to higher temperatures (>1000°C) compared to Cr-Al-Y-N (~900°C), thus enhancing the alloy thermal stability. The improved thermal stability may be attributed to increased cohesive energie, as revealed from *ab initio* calculations.

This work was supported by the Slovak Research and Development Agency [Grant No. APVV-17-0320]

10:20am **B5-2-FrM-8 Interface Characteristics Between PVD- AlTiN and Electroplated Hard Chrome by Duplex Process**, *D Wang,* MingDao University, Taiwan*; **Li-Chi Hsu**, J Hung,* Aurora Scientiftic Corp., Canada*; C Chen, H Liu,* Surftech Corp., Taiwan*; W Ho,* MingDao University, Taiwan

Most of the hard coatings have good corrosion resistance on certain applications. The traditional way for corrosion resistance accepted by industries are electroplated hard chrome. However, in some severe environment, hard chrome can not pass corrosion tests, as a result, PVD hard coatings are applied on hard chrome to even further enhance corrosion resistance in some special applications. In this research, we are investigating the unique application of cathodic arc technology in depositing AlTiN hard coating film onto electroplated hard chrome PH17-4 stainless steel 1-inch OD shafts. The requirement for the AlTiN multi-layer coating is to take into consideration of residual stress between the hard chrome layer and AlTiN coating to ensure great adhesion between two materials. Also, the residual chemicals from hard chroming process will be analyzed and the removal of chromium oxide will be addressed in both pre-coating cleaning and in-chamber cleaning processes. This research will reveals the effect of coating process on the sensitive to temperature of the duplex coatings which related to the residual stress. Meanwhile, it is critical to monitor whether any released on the hard chrome surface, causing contamination of chrome surface in the coating process. Results of this research will enhance corrosion resistance by applying both hard chrome and hard coating by PVD cathodic arc process.

10:40am **B5-2-FrM-9 Manipulation of Bimodal Matrix in Plasma Sprayed Nanostructured YSZ Coating and Its Effect on the Microstructure***, **Pavan Bijalwan,*** Tata Steel Limited, India*; A Islam, K Pandey,* Indian Institute of Technology, India*; A Pathak, M Dutta,* Tata Steel Limited, India*; A Keshri,* Indian Institute of Technology, India

Nanostructured YSZ (n-YSZ) based ceramic TBCs have attracted widespread attention because of the exceptionally higher toughness, bond strength and thermal cycling life compared to the conventional YSZ. However, the primary concern is to control the melting of nanostructured powders in the plasma jet by adjusting the plasma spray parameters, resulting the formation of the bimodal structured coatings. Further, by controlling the size, shape, and morphology of the nanozones, it is possible to engineer coatings with enhanced properties. There is a complete scarcity in correlating the effect of the content of nanostructured zone on the performance of the coating. In this work, attempts have been made to control the melting states of nanoparticles by changing the plasma process parameters and to manipulate the different contents of nanozones in the coating. Temperature and velocity profile of the in-flight particle was captured at several plasma process parameters using Accuraspray in-flight particle diagnostic sensor. Free standing coating will be synthesized after analyzing the temperature and velocity profile of the in-flight particle. These free-standing coating will be evaluated in detail for the porosity and the bimodal matrix. At the optimized parameter, final coating will be fabricated and various abovementioned properties will be evaluated.

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