Protective and High-temperature Coatings
Room Town & Country D - Session MA3-2-MoA

Hard and Nanostructured Coatings II

Moderators: Marcus Günther, Robert Bosch GmbH, Germany, **Rainer Hahn**, TU Wien, Institute of Materials Science and Technology, Austria, **Stanislav Haviar**, University of West Bohemia, Czechia, **Fan-Yi Ouyang**, National Tsing Hua University, Taiwan

1:40pm **MA3-2-MoA-1 In Operando Studies of Hard Coatings Using High-Energy X-Ray Diffraction***, Lina Rogström (lina.rogstrom@liu.se),* Linköping University, IFM, Sweden **INVITED**

Wear resistant coatings covering tools used for metal machining experiences tough conditions during application, such as high temperatures and stresses. The detailed nature of tool wear is still largely unknown. One limitation to access the material behavior in the contact zone between the tool and the workpiece is the lack of line-of-sight to this area. The contact zone is in the order of 1 mm^2 and characterized by steep gradients in temperature and stress. The material behavior is thus expected to vary significantly within the contact zone, why local analysis is crucial to understand the relation between material properties and wear behavior. Due to the complex situation, model studies at high temperature and/or pressure do not provide a full understanding of the material behavior, instead, real-time methods to access the contact area are needed.

High-energy x-rays are highly suitable for studies of the hidden contact area between tool and workpiece since they can penetrate several mm of coating and workpiece, and in some case also the substrate material. TiAlN is one of the most common materials for wear resistant coatings. It's favorable mechanical properties at high temperatures are related to the spinodal decomposition of the fcc-TiAlN phase, the details of which successfully have been characterized by high-energy x-ray scattering techniques [1].

To study the tool in real time during metal machining, we have designed a small-scale lathe that can be placed at the high-energy materials science x-ray beamline P07 at Petra III [2]. The lathe allows for longitudinal and orthogonal turning using industrial tooling systems and is built for industrial cutting parameters such as cutting speed and feed. Its design enable access to the tool-chip interface with an x-ray beam during turning. In this presentation, results will be presented from in operando experiments performed (i) with the x-ray beam parallel to the tool flank side and (ii) with the x-ray beam parallel to the tool rake face. The results will be discussed in terms of possibilities and limitations of in operando high-energy x-ray diffraction techniques to access the material behavior in real time during metal machining.

[1] M. Odén, L. Rogström et al., Appl. Phys. Lett. 94, 053114 (2009); L. Rogström et al., Thin Solid Films 520, 5542 (2012); A. Knutsson, L. Rogström et al., J. Appl. Phys. 113, 213518 (2013); N. Norrby, L. Rogström et el., Acta Mater. 73, 205 (2014).

[2] L. Rogström et al., Rev. Sci. Instr., 90, 103901 (2019); L. Rogström et al., Submitted for publication (2023).

2:20pm **MA3-2-MoA-3 Exploring High Temperature Decomposition and Age Hardening in Wurtzite $Ti_{1-X}Al_XN_Y$ (X=0.75 to 0.98, Y=0.82 to 1) Thin Films***, Janella Mae Rosario Salamania (janella.salamania@secotools.com),* Seco Tools AB, Sweden*; F. Bock,* Linköping University, Sweden*; L. Johnson, K. Calamba Kwick, I. Schramm,* Sandvik Coromant, Sweden*; A. Farhadizadeh,* Linköping University, Sweden*; T. Hsu,* Sandvik Coromant, Sweden*; F. Tasnadi, I. Abrikosov, L. Rogström, M. Odén,* Linköping University, Sweden

Wurtzite TiAlN is an intriguing material. It forms in high Al-content industrial grade tool coatings and has potential as a semiconductor with adjustable band gap and can serve as an insulating motif for superconductors and piezoelectric crystals. The characterization of wurtzite TiAlN poses challenges due to the difficulty in synthesizing them as single-phase solid solutions. As a consequence, its thermodynamic and elastic properties are not determined, and the influence of high-temperature and crystallographic defects are unknown.

The research presented here explores the properties and behaviors of wurtzite TiAlN alloys. It covers the challenges associated with synthesizing single-phase solid solutions of wurtzite TiAlN and the unknown thermodynamic, elastic properties, and high-temperature behavior of wurtzite $Ti_{1-x}Al_xN$. First-principles calculations were used to predict a phase diagram encompassing miscibility gaps and spinodals for both cubic and wurtzite $Ti_{1-x}Al_xN$ and the full elasticity tensor. Metastable stoichiometric wurtzite $Ti_{1-x}Al_xN$ films with varying Al content were grown by arc deposition using pulsed bias voltage at a low-duty cycle. High-temperature annealing induced spinodal decomposition in the wurtzite $Ti_{1-x}Al_xN$, resulting in nanoscale compositional modulations and age hardening of 1-2 GPa.

The high-temperature behavior of wurtzite TiAlN is affected by the presence of nitrogen vacancies. To study this in HRSTEM we grew nitrogen-deficient epitaxial wurtzite $Ti_{1-x}Al_xN_y$y films, which revealed decomposition into intermediary MAX-phases, segregating into c-TiN, w-AlN phases, and TiAl nanoprecipitates after high-temperature annealing. The semi-coherent interfaces between the wurtzite phase and precipitates contribute to age hardening of approximately 4-6 GPa, persisting even after annealing at 1200°C. This study sheds light on how nitrogen vacancies impact the decomposition and mechanical properties of wurtzite TiAlN, offering valuable insights into the behavior of these materials under extreme conditions.

2:40pm **MA3-2-MoA-4 Enhancing the Thermal Stability of $V_{0.25}Al_{0.25}N_{0.50}$ by Oxygen Incorporation***, Matej Fekete (fekete@physics.muni.cz), D. Neuß, M. Hans, G. Nayak,* RWTH Aachen University, Germany*; Z. Czigány,* Center for Energy Research, Hungary*; S. Karimi Aghda,* RWTH Aachen University, Germany*; D. Primetzhofer,* Uppsala University, Sweden*; J. Sälker, J. Schneider,* RWTH Aachen University, Germany

Thermal stability and mechanical behavior are key criteria for the design of the next generation of protective coatings. Today, transition metal aluminum nitrides are benchmark coatings on tools and components because of their combined thermal, chemical, and mechanical stability.

To enhance the thermal stability of metastable fcc NaCl-type $V_{0.25}Al_{0.25}N_{0.50}$ coatings, oxygen is integrated into the material system. High power pulsed magnetron sputtering at 450°C is utilized to synthesize metastable fcc $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ coating and reference $V_{0.25}Al_{0.25}N_{0.50}$. Coatings are annealed in a vacuum for 30 minutes to up to 950 °C and 1300 °C for $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively.

Decomposition of V and Al within the nitride phase is observed to start at 800 and 900 °C in $V_{0.25}Al_{0.25}N_{0.50}$ and $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$, respectively, although a formation of a few nm scale aluminum-rich regions in as deposited $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ is detected by atom probe tomography. Selected area electron diffraction data reveal the presence of wurtzite phase in the $V_{0.25}Al_{0.25}N_{0.50}$ annealed at 950 °C, while in $V_{0.25}Al_{0.25}O_{0.11}N_{0.39}$ annealed at 1300 °C no secondary phase is detected. The thermal stability enhancement by oxygen incorporation can be understood based on the magnitude of the relevant migration barriers as well as the formation energies for vacancies.

3:00pm **MA3-2-MoA-5 Interplay of Substrate Template Effects and Bias Voltage Regarding the Microstructure of Cathodic Arc Evaporated fcc-$Ti_{0.5}Al_{0.5}N$ Coatings***, Michael Tkadletz (michael.tkadletz@unileoben.ac.at), N. Schalk, H. Waldl,* Montanuniversität Leoben, Austria*; B. Sartory, J. Wosik,* Materials Center Leoben Forschung GmbH, Austria*; J. Keckes, J. Todt,* Montanuniversität Leoben, Austria*; M. Burghammer,* European Synchrotron Radiation Facility, France*; C. Czettl,* CERATIZIT Austria GmbH, Austria*; M. Pohler,* Ceratizit Austria GmbH, Austria

Ever since the implementation of hard coatings as wear protection for cutting tools, their microstructural design has been of major interest. While the effect that deposition parameters such as the applied bias voltage or the substrate temperature have on the microstructure are frequently investigated and rather well understood, commonly less attention is paid to the used cemented carbide substrates. Yet properties like their phase composition and carbide grain size significantly influence the resulting coating microstructure. Thus, within this work, substrate template effects are studied on fcc-$Ti_{0.5}Al_{0.5}N$ coatings grown by cathodic arc evaporation onto cemented carbide substrates with different WC grain sizes. A systematic variation of the bias voltage resulted in coarse, intermediate and fine grained coating microstructures, which revealed substrate template-based coating growth at low bias voltages and bias dominated coating growth at high bias voltages. In addition, a strong influence of the applied bias voltage on the resulting preferred orientation of the deposited coatings was observed, providing the basis to tailor their fiber texture to <100>, <110> or <111>. Elaborate X-ray diffraction and electron microscopy studies contributed to gain further understanding of the substrate template effects and revealed that implementation of a suitable base layer offers the possibility to effectively prevent any influence of the used substrate on the microstructural evolution of the coating. The obtained results set the fundament to implement tailored microstructures with designed gradients of crystallite size, preferred orientation and consequently mechanical properties, which, as required, either utilize substrate template effects or avoid them.

3:20pm **MA3-2-MoA-6 Decomposition of Single Crystal $Hf_{1-x}Al_xN$ Films Grown at High Temperatures and the Effect on Mechanical Properties**, ***Marcus Lorentzon (marcus.lorentzon@liu.se)***, Linköping Univ., IFM, Thin Film Physics Div., Sweden; *T. Zhu,* Nagoya University, Japan, China; *N. Takata,* Nagoya University, Japan; *S. Nayak, J. Palisaitis, G. Greczynski,* Linköping Univ., IFM, Thin Film Physics Div., Sweden; *J. Rosen,* Linköping University, IFM, Sweden; *J. Birch, N. Ghafoor,* Linköping Univ., IFM, Thin Film Physics Div., Sweden

TM-Al-N is an important class of ceramic coating materials that exhibit excellent functional properties. The well-studied TiAlN material system has a high hardness and elastic modulus, good thermal stability, low electrical resistivity, and can also work as diffusion barriers. A similar material, but much less studied, HfAlN offers potential for high-temperature applications thanks to the extreme temperature stability of HfN with a melting point of ~3300°C. In this study we have grown single crystal cubic $Hf_{1-x}Al_xN_y$ on MgO(001) substrates at 800°C using reactive magnetron co-sputtering from elemental Hf and Al targets. A high flux (J_{ion}/J_{metal}>9.2) of low energy (20 eV < E_{ion} <26 eV) ion assistance was employed with -30V substrate bias. An improved crystalline quality of HfAlN films was obtained on adding up to 30 at.% Al. Similar to the case of annealed TiAlN [1], characteristic spinodal decomposition (in this case surface initiated during growth), with striking check-patterned lattice of AlN-rich and HfN-rich domains is observed in lattice-resolved STEM imaging and confirmed by characteristic satellite reflections in synchrotron wide-angle x-ray scattering and in selected area electron diffraction. Thanks to the nanosized compositional modulations, the nanoindentation hardness of the films showed a substantial increase from 26 GPa to 40 GPa on adding 6 to 30 at.% Al in the HfAlN film which is lower concentrations than previously reported [2]. The fracture mechanics of $HfN_{1.22}$ and $Hf_{0.93}Al_{0.07}N_{1.15}$ films studied by micropillar compression testing showed unusual ductile behavior with uniform deformation and substantial strain hardening in the HfN film, contrary to the characteristic catastrophic brittle failure common for ceramics. When alloying with Al the pillars attain catastrophic failure on activation of a single slip system {111}<011>, although a substantially higher stress is required for the shear failure. We will uncover the microscopic origin of the non-characteristic (but beneficial) ductile behavior of $HfN_{1.22}$ in relation to the stoichiometry of the film and point defect formation, in particular anti-site point defects which affect the physical properties of HfN_y[3]. We will highlight the impact of increasing Al content on the size of the check-patterned modulation in the cubic phase films and preliminary results of spinodal decomposition in high Al-content wurtzite $Hf_{0.59}Al_{0.41}N_{1.23}$.

[1] P. H. Mayrhofer *et al.*, *Appl. Phys. Lett.*, vol. 83, no. 10, Sep. 2003

[2]B. Howe *et al.*, *Surface and Coatings Technology*, vol. 202, no. 4, Dec. 2007

[3]H.-S. Seo *et al.*, *Journal of Applied Physics*, vol. 97, no. 8, Apr. 2005

4:00pm **MA3-2-MoA-8 Influence of the Thickness of TiAlSiN on the Thermal Properties as Input Parameter for FEM–Simulation**, *K. Bobzin, C. Kalscheuer,* ***Nina Stachowski (stachowski@iot.rwth-aachen.de)***, Surface Engineering Institute (IOT) - RWTH Aachen University, Germany; *B. Breidenstein, B. Bergmann, F. Grzeschik,* Institute of Production Engineering and Machine Tools (IFW) - Leibniz Universität Hannover, Germany

Hard coatings like TiAlN deposited by physical vapor deposition are state of the art for wear and oxidation protection of cutting tools. The cutting performance depends on coating material and process as well as cutting edge microgeometries. Both have an influence on the thermomechanical tool loads resulting in tool wear. Therefore, for a process adapted design, the consideration of the entire system is necessary. One approach to substitute costly machining investigations and save material resources is the use of Finite Elemente (FE)-based chip formation simulations. However, in order to perform these simulations, information about chemical, thermal and physical coating behavior in the temperature range relevant for machining is necessary. In the present study, nanocomposite TiAlSiN coatings with varying coating thicknesses were deposited on cemented carbide tools by HPPMS /dcMS processes. The effect of coating thickness on coating morphology, chemical composition, thermal diffusivity as well as indentation hardness and indentation modulus at θ = 20 °C, θ = 200 °C,θ = 400 °C and θ = 600 °C was analyzed. Additionally, the distribution of the heat, generated during turning 42CrMo4+A was simulated for the coated cutting tool as preliminary step for the chip formation simulation. A columnar morphology with constant chemical composition was determined for all coating variants. While the arithmetic mean value of the coating roughness increased with increasing coating thickness, there was no influence of coating thickness on thermal diffusivity and high temperature coating hardness measurable. Nevertheless, an influence on the tool temperature can be observed in the application behavior in turning tests as well as in the simulation. As a possible cause, the contact conditions change due to a larger cutting edge microgeometry caused by a higher coating thickness, which leads to a higher temperature. The present results show that by dimensioning the tested TiAlSiN hard coating, no influence of the selected coating thickness on properties such as thermal diffusivity and the indentation hardness of the coating has to be considered. An individual adaptation of the coating thickness within a range of 2 µm ≤d_s ≤ 6 µm to the tool geometry is therefore easily possible for the investigated TiAlSiN coatings without further modification of the coating.

4:20pm **MA3-2-MoA-9 Non-Reactive Magnetron Sputtering of Ti-Al-N Coatings**, ***Balint Hajas (balint.hajas@tuwien.ac.at)***, *S. Bermanschläger, T. Wojcik,* TU Wien, Institute of Materials Science and Technology, Austria; *D. Primetzhofer,* Uppsala University, Angstrom Laboratory, Sweden; *S. Kolozsvari,* Plansee SE, Germany; *P. Mayrhofer,* TU Wien, Institute of Materials Science and Technology, Austria

Hard protective coatings allow for increased lifetime of machining tools and more versatile applications. Although (Ti,Al)N coatings have a rich history in material science with various improvements for their production, little is known about their non-reactive deposition using Ti-Al-N compound targets.

Reactive deposition of such (Ti,Al)N coatings is studied in-depth, showing that especially for sputtering the resulting microstructure and consequently properties (next to deposition rate) hugely depend on the N_2-partial pressure used. Alternatively, such nitrides can also be prepared non-reactively using nitride compound targets. Here, we use powder metallurgically prepared TiN–AlN compound targets with either 50, 66, or 80 mol% AlN to prepare (Ti,Al)N coatings with various chemical composition through non-reactive DC as well as pulsed DC magnetron sputtering.

The primary investigations focused on how the mechanical properties such as hardness and indentation modulus depend on various deposition conditions, such as sputtering power density, pulse frequency, substrate temperature, substrate-to-target distance, and magnetron condition. Detailed investigations by X-ray diffraction showed that while all (Ti,Al)N coatings obtained from the $(TiN)_{0.5}(AlN)_{0.5}$ target were single-phase face centered cubic (fcc) structured those obtained from the $(TiN)_{0.2}(AlN)_{0.8}$ target were single-phase hexagonal close packed (hcp) wurtzite-type structured. The hcp-phase fraction within the (Ti,Al)N coatings prepared with the $(TiN)_{0.34}(AlN)_{0.66}$ target strongly depends on the deposition conditions. The maximum hardness of the fcc-(Ti,Al)N coatings was ~38.2 GPa, and that of the hcp-(Ti,Al)N coatings was 29.3 GPa. When compared with the reactive deposition of fcc-(Ti,Al)N using similar deposition conditions, the non-reactive route allows for a doubled deposition rate, thus contributing to reducing energy consumption for their preparation.

4:40pm **MA3-2-MoA-10 nc-Sic/a-C Coating for Industrial Applications**, ***Mojmir Jilek (jilek.jr@shm-cz.cz)***, *O. Zindulka,* SHM sro, Czechia; *Z. Studeny,* University of Defence, Czech Republic

Silicon carbide is one of the hardest materials. In the form of thin layers, it is prepared primarily using CVD technology.

Presented PVD deposition technology (rotary sputtering of segmented targets with high power) allows deposition of SiC based coatings with hardness higher than 60GPa more than 10um thick. This coating shows nanocrystalline composite structure of nc-SiC/a-C.

In cutting test, our coating achieved 60% lifetime compared to thick diamond layer. In contrast to diamond layer, the SiC coating deposition is simpler and coated tools can also be easily reground, or chemically decoated.

5:00pm **MA3-2-MoA-11 Synthesis and Investigation of Crystalline (Ta,Al)B_2 and AlB_2 Thin Films***, Chun Hu (chun.hu@tuwien.ac.at)*[8]*, S. Lin,* Institute of Materials Science and Technology, TU Wien, Austria*; P. Pöllmann, S. Mráz,* RWTH Aachen University, Germany*; T. Wojcik,* Institute of Materials Science and Technology, TU Wien, Austria*; J. Schneider,* RWTH Aachen University, Germany*; N. Koutná, P. Mayrhofer,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal diboride thin films are promising functional materials with outstanding mechanical properties and thermal stability. However, development of magnetron-sputtered TMB_2 thin films is challenging, since their composition typically deviates from 1:2 metal-to-boron stoichiometry. We developed $(Ta_{1-x}Al_x)B_y$ (x=0–0.48, y=1.23–2.29) thin films and use Ta-Al-B as a model system to study the correlation of microstructure, boron stoichiometry, and mechanical properties implementing experimental and computational materials science. The proposed reasons for off-stoichiometry include angular distribution of the sputtered species, their scattering in the gas phase, re-sputtering and potential evaporation from the grown films for the complex evolution of film compositions, as well as energetic preference for vacancy formation and competing phases as factors for governing the phase constitution. The changes in stoichiometry correlate with the evolution of microstructure, hardness, and elastic modulus. Increasing y from 1.23 to 1.64 leads to the highest hardness (38.8 GPa) among $(Ta_{1-x}Al_x)B_y$ studied here due to promoted formation of the AlB_2-prototype phase. $(Ta_{1-x}Al_x)B_y$ with y=1.97-2.29, corresponding to x up to 0.48, reveal gradually decreasing hardness (down to 31.3 GPa) due to the increased AlB_2-fraction. Complementing the studies for $Ta_{1-x}Al_xB_y$ solid solutions, we also synthesized crystalline AlB_x (x = 1.99, 1.97, 2.27) thin films and studied mechanical properties, thermal stability, and oxidation resistance. This is the first report about AlB_2 thin films with an AlB_2-prototype crystal structure, which is difficult to crystallize due to the close-to-zero formation energy. The $AlB_{2.27}$ thin film shows an exceptional oxidation resistance with an onset temperature of ~1000 °C.

5:20pm **MA3-2-MoA-12 Tribocorrosion and Biocompatibility Analysis of Carbide-derived Carbon (CDC) Surface Modification for Hip Implants***, Yani Sun (ysun98@uic.edu)*[8]*, H. Kanniyappan, M. Karunanidhi, M. Daly, M. McNallan, M. Mathew,* University of Illinois at Chicago, USA

Total hip replacement (THR) suffers from inferior tribocorrosion damage, which may lead to the premature failure of hip implants. Carbide-derived carbon (CDC) is a carbon material derived from carbide precursors. Previously, we have proved that CDC can effectively protect Ti6Al4V from tribocorrosivedamages under open-circuit potential (OCP). Nonetheless, some fundamental properties and biological analysis of CDC are still lacking. Therefore, this study aims to characterize CDC’s thickness and biological responses before and after tribocorrosion tests to evaluate CDC as a biomaterial.

CDC was synthesized on the Ti6Al4V disk (11 mm dia x 7 mm) by electrolysis method and confirmed by Raman spectroscopy. Prior to the experiments, the control group Ti6Al4V disks were polished with a mirror finish (Ra<50 nm). The tribocorrosion testing was conducted on a customized reciprocal sliding (±2 mm) tribocorrosion system at 1 Hz for 3600 cycles, which was connected to a Gamry potentiostat. Bovine calf serum (BCS) with 30 g/L proteins was selected as the electrolyte to simulate human body fluid. Three electrodes were used where the working electrode is the sample, the counter electrode is a graphite rod, and the reference electrode is a standard calomel electrode (SCE). The electrochemical protocol was followed with three stages, which are (i) initial stabilization with OCP, (ii) tribocorrosion stage with OCP and potentiostatic (PS), and (iii) final stabilization with OCP. To measure thickness, a diamond saw sectioned the disk, and the ion-milled section was examined under SEM with EDS. MG-63 human osteoblast-like cells were employed to test the cytocompatibility of CDC, and the cell viability was quantified using the Alamar blue assay. Also, the bioactivity of CDC was studied with 4',6-diamidino-2phenylindole (DAPI) staining assay live/dead assay.

As a result, the produced CDC shows an excellent tribocorrosion performance, presenting around 30-fold lower potential variation than Ti6Al4V. Also, the CDC was detected by Raman spectroscopy and found under SEM at the wear scar even after the tribocorrosion test. Interestingly, a carburized layer of approximately 5 um was observed; however, a distinct layer of CDC was not showing under SEM. Regarding the biocompatibility analysis, no significant difference was found in CDC’s cell proliferation compared to the control group Ti6Al4V, and living cells were shown on the sample. According to the amount and the cell shapes, no noticeable difference was found between CDC and the Ti6Al4V, verifying CDC's biocompatibility on the Ti6Al4V substrate.

[8] **Graduate Student Award Finalist**

[8] **Graduate Student Award Finalist**

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