Protective and High-temperature Coatings
Room Golden State Ballroom - Session MA-ThP
Protective and High-temperature Coatings Poster Session

MA-ThP-1 High Temperature Fracture Characteristics of Si Containing Ternary and Quaternary Transition Metal Diborides*, **Anna Hirle [anna.hirle@tuwien.ac.at]**, Ahmed Bahr, Rainer Hahn, Tomasz Wojcik,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria*; Szilard Kolozsvári, Peter Polcik,* Plansee Composite Materials GmbH, Germany*; Jürgen Ramm, Carmen Jerg,* Oerlikon Surface Solutions AG, Liechtenstein*; Helmut Riedl,* Christian Doppler Laboratory for Surface Engineering of High-performance Components, TU Wien, Austria

To enhance the restricted oxidation resistance of transition metal diboride (TMB) ceramics, alloying with Si and disilicide phases is an effective method, resulting in the formation of highly dense and protective SiO_2 scales. This phenomenon has been well documented in the context of bulk ceramics [1, 2], and recent studies have also corroborated its occurrence in thin-film TMBs, including CrB_2, HfB_2, and TiB_2 [3, 4]. The incorporation of Si, $TaSi_2$ or $MoSi_2$ into TiB_2 results in a significant reduction in oxidation kinetics, while exhibiting only minor effects on the mechanical properties. In the case of quaternary TiB_2-based coatings, hardness values of 36 GPa ($TaSi_2$) and 27 GPa ($MoSi_2$) have been achieved, in comparison to approximately 38 GPa for the binary system. All of the aforementioned coatings exhibited α-AlB_2 crystal structure, with a preferred (0001) orientation being a key factor in achieving the highest hardness. Nevertheless, the fracture characteristics of these Si-alloyed TMBs remain largely unexplored.

The objective of the present study is to elucidate the fracture characteristics, particularly K_{IC}, of these Si-containing TMBs at elevated temperatures up to 850 °C through the application of in-situ micromechanical testing techniques. Accordingly, a series of Ti-TM-Si-$B_{2\pm z}$ coatings was deposited via non-reactive DC magnetron sputtering using a variety of composite targets, including TiB_2, $TiB_2/TiSi_2$ (90/10 & 80/20 mol%), $TiB_2/TaSi_2$ (90/10 & 80/20 mol%), and $TiB_2/MoSi_2$ (85/15 & 80/20 mol%). To gain a deeper understanding, additional detailed structural investigations were conducted using X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), and elastic recoil detection analysis (ERDA).

In comparison to the binary TiB_{2+z} and the quaternary Ti-Ta-Si-$B_{2\pm z}$, the Si and $MoSi_2$-containing coatings exhibited a distinct onset of plastic deformation at approximately 600 °C. This phenomenon can be attributed to the precipitation of silicon-containing phases, which underlines the significance of conducting material testing at temperatures relevant to their intended applications.

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MA-ThP-3 Spinodal Decomposition and Nano-precipitate Formation in Ag-modified High-Entropy Alloys*, **Salah-eddine Benrazzouq [salah-eddine.benrazzouq@univ-lorraine.fr]**, Abdelkrim Redjaimia, Jaafar Ghanbaja, Sylvie Migot, Valentin A. Milichko, Jean-François Pierson,* Institut Jean Lamour - Université de Lorraine, France

Phase separation in multi-component alloys presents both challenges and opportunities for material design. While traditionally viewed as a limitation, controlled phase separation could enable unique microstructural features and enhanced properties. High-entropy alloys (HEAs) have garnered significant attention across various research fields owing to their exceptional properties. This study investigates the distinctive behavior of silver addition to the CrMnFeCoNi Cantor alloy, where silver's higher mixing enthalpy creates an interesting case of spinodal decomposition and nano-precipitate formation.

Using DC magnetron co-sputtering, we synthesized CrMnFeCoNiAg thin films with systematically varied silver content. X-ray diffraction (XRD) patterns reveal distinct non-mixing behavior with the emergence of pronounced peaks corresponding to both silver and Cantor alloy phases. Cross-section bright-field TEM micrograph and SAED patterns revealed a dense structure with Ag precipitates dispersed throughout the 900-nm-thick film. HRTEM micrographs showed a nanoprecipitate morphology with fine-scale linear precipitates, while STEM-HAADF imaging highlighted the internal structure, revealing characteristic modulated patterns with striations parallel to the basal plane, indicative of spinodal decomposition with cuboidal particles and tweed-like contrast patterns.

The controlled formation of these nano-precipitates and their unique distribution pattern suggests potential for mechanical property enhancement through precipitation strengthening mechanisms. Our findings demonstrate how controlled phase separation can be used to engineer microstructure in HEA thin films. This understanding provides new strategies for designing multi-functional materials through deliberate exploitation of immiscibility effects, advancing our knowledge of phase evolution in complex alloy systems and offering pathways for property optimization in advanced coating applications.

MA-ThP-4 Influence of Si Content on Cracking Behavior of CrAlSiN Coatings*, Kirsten Bobzin, Christian Kalscheuer, **Max Philip Möbius [moebius@iot.rwth-aachen.de]**, Jessica Borowy,* Surface Engineering Institute - RWTH Aachen University, Germany

The increasing demands for workpiece quality and cost-effectiveness in machining processes necessitate a comprehensive consideration of all relevant factors, including cutting parameters, materials, tool coatings, and geometry. Physical Vapor Deposition (PVD) manufactured CrAlSiN nanocomposite coatings, composed of CrAlN grains in a SiN_x matrix, represent a promising solution for improved tool life of milling tools. The elastic-plastic properties of the coating and the deformation behavior of the material composite thereby can be deliberately influenced by varying the silicon content.

CrAlSiN coatings with silicon contents of x_{Si} = 10, 15, 20, and 25 at.-% in the metal portion were fabricated on cemented carbide WC-Co substrates. The indentation hardness H_{IT} and indentation modulus E_{IT} of the coatings were measured through nanoindentation (NI) with a force of F_{NI} = 10 mN, using a Berkovich indenter. Additionally, crack resistance was evaluated using quasi-static high load (HL) nanoindentation tests under forces ranging from F_{HL} = 750 to 1,750 mN, with increments of ΔF_{HL} = 250 mN. A conical diamond indenter was used for the high load nanoindentation tests. The resulting indents were subsequently analyzed using scanning electron microscopy (SEM). The findings reveal that the indentation hardness H_{IT} remains unchanged at H_{IT} = (25.48 ± 1.59) GPa, while the indentation modulus increases with higher silicon content, ranging from E_{IT} = (222.64 ± 10.45) GPa for x_{Si} = 10 at.-% up to E_{IT} = (239.89 ± 7.78) GPa for x_{Si} = 20 at.-%. After high load nanoindentation all coatings exhibit no cracks at F_{HL} = 750 mN. With F_{HL} ≥ 1,000 mN on the other hand cracks can be observed in all coatings. Nevertheless, with rising silicon content, the maximum indentation depth h_{max} decreases, while the residual indentation depth h_0 remains constant. Furthermore, the proportion of plastic work shows a slight reduction as silicon content x_{Si} increases. These results indicate that the resistance against plastic deformation of the CrAlSiN coating increases with higher silicon content.

Coatings with high silicon content demonstrate promising resistance against plastic deformation at room temperature, highlighting their potential for further investigation. This initial test qualifies these coatings for additional studies under high-temperature conditions, aiming to enhance their applicability in machining processes. The insights gained from this research could lead to the development of more durable and efficient cutting tools, ultimately improving productivity in industrial applications.

MA-ThP-5 Relationship between Optical and Electrical Properties and the Microstructure of High Entropy Nitride (TiVZrNbTa)N_X Thin Films*, **Miguel Piñeiro [miguel.pineiro-sales@univ-lorraine.fr]**,* Institut Jean Lamour - Université de Lorraine, France, Peru*; Salah-Eddine Benrazzouq,* Institut Jean Lamour - Université de Lorraine, France, Morocco*; Alexandre Bouché, Valentin Milichko, David Pilloud, Thomas Easwarakhanthan,* Institut Jean Lamour - Université de Lorraine, France*; Frank Mücklich,* Saarland University, Germany*; Jean-François Pierson,* Institut Jean Lamour - Université de Lorraine, France

In this study, high entropy nitride TiVZrNbTa thin films were prepared by DC reactive magnetron sputtering on silicon substrates at room temperature. The impact of varying nitrogen flow rateson the structural, microstructural, optical and electrical properties were investigated. X-ray diffraction technique revealed that all the deposited films exhibited a polycrystalline structure with fcc phase. However, the pure metallic samples displayed an amorphous structure [1]. Optical properties analysis showed a decrement of the reflectance compared with free-nitrogen sample in the infrared region, as determined by UV-VIS spectroscopy [2]. Hall-effect measurements indicate that the electrical resistivity for all samples remained within the range between 100 and 300 μΩ cm. Interestingly, samples deposited with applied substrate bias power during the deposition process did not show a significant change in resistivity. This suggests that substrate biasing has minimal effect on the electrical transport properties of the latter films. On the other hand, applying adjustable substrate bias led to a blueshift in the epsilon-near-zero (ENZ) wavelength. Furthermore, X-ray photoelectron spectroscopy (XPS) shows the effect of the nitrogen flow rate on the residual stress [3] and plasmon frequency. The impact of varying nitrogen flow rates on the microstructural properties were further investigated and explained.

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MA-ThP-6 Microstructure Evolution and Oxidation Behavior of Diffusion Pt-γ/γ' and Pt-aluminide Coatings at 1200 °C*, **Radoslaw Swadzba [radoslaw.swadzba@git.lukasiewicz.gov.pl]**, Agnieszka Sasiela,* Lukasiewicz Research Network - Uppersilesian Institute of Technology, Poland*; Boguslaw Mendala, Lucjan Swadzba,* Silesian University of Technology, Poland*; Lukasz Pyclik, Michal Gut,* Avio Polska sp. z o. o., Poland

This study examines the microstructural evolution and oxide scale growth of Pt-γ/γ' and Pt-aluminide diffusion coatings applied to a second-generation single-crystal Ni-based superalloy at 1200 °C. The Pt-γ/γ' coatings were produced through platinum electroplating followed by a 2-hour diffusion heat treatment at 1079 °C. Subsequently, Vapor Phase Aluminizing (VPA) at 1079 °C for 6 hours generated Pt-modified aluminide coatings. Both coating types were subjected to Thermogravimetric Analysis (TGA) in air for 20 hours as well as cyclic oxidation test up to 300 1-hour cycles at 1200 °C.

The initial and oxidized coatings were characterized using Electron Backscatter Diffraction (EBSD) to analyze phase transformations, grain size evolution, and interdiffusion between the coatings and the substrate alloy. In the as-deposited state, the Pt-γ/γ' coating consisted of γ and γ' grains enriched in Pt, with a thickness of approximately 27 µm, while the Pt-aluminide coating exhibited an outer zone of $PtAl_2$ and β-NiAl phases. During the high temperature oxidation testing, the Pt-γ/γ' coating showed grain growth and Pt diffusion to a depth of approximately 70 µm after 20 hours. The Pt-aluminide coating underwent martensitic transformation in its outer layer, with Al-depleted β-NiAl in its middle region and an interdiffusion zone containing Cr-rich precipitates.

High-resolution Scanning Transmission Electron Microscopy (STEM) provided detailed characterization of the alumina oxide scales formed on both coatings, revealing information on oxide grain size and the segregation of reactive elements (RE) to grain boundaries.

MA-ThP-7 Unprecedented B Solubility in Cubic (Hf,Ta,Ti,V,Zr)B-C-N Coatings*, Andreas Kretschmer,* TU Wien, Austria*; Marcus Hans, Jochen Schneider,* RWTH Aachen University, Germany*; **Paul Mayrhofer [paul.mayrhofer@tuwien.ac.at]**,* TU Wien, Institute of Materials Science and Technology, Austria

We investigate the influence of compositional complexity in Ti-B-C-N-based coatings by depositing Ti-rich (Hf,Ta,Ti,V,Zr)B-C-N coatings with varying B/C ratios (from 0/21 to 32/0 at%). Despite the high B content of 32 at% in the C-free material, this $(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_{0.6}N_{0.4}$ forms a single-phase fcc solid solution without a boride tissue phase. All coatings—$(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_xC_{0.5-x}N_{0.5}$ with x = 0.2, 0.3, 0.4, $(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_{0.6}N_{0.4}$, and $(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})C_{0.4}N_{0.6}$—exhibit similar hardness values of 37–38 GPa, but increasing B content leads to a decreasing indentation modulus. This trend is supported by *ab initio* calculations of fcc-$(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_xC_{0.5-x}N_{0.5}$ (for x = 0, 0.125, 0.25, 0.375, 0.5), which also confirm the stability of these solid solutions over a wide compositional range. Despite increasing chemical complexity, the addition of B and C has little effect on lattice distortion.

Among the investigated coatings, $(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_{0.4}C_{0.1}N_{0.5}$ provides the best balance between high hardness (37.7±1.0 GPa) and fracture toughness (K_{IC} = 4.0±0.5 MPa·m$^{0.5}$). This compositionally complex, single-phase, fcc-structured Ti-rich (Hf,Ta,Ti,V,Zr)B-C-N retains its hardness—which even slightly increases to 38.3±1.3 GPa—upon vacuum annealing up to 1200 °C. X-ray diffraction and atom probe tomography confirm its high-temperature phase stability, as an hcp-TiB_2-based phase forms only upon annealing beyond 1200 °C. More generally, all $(Hf_{0.1}Ta_{0.1}Ti_{0.6}V_{0.1}Zr_{0.1})B_xC_{0.5-x}N_{0.5}$ coatings with x = 0.2, 0.3, and 0.4 exhibit a total configurational entropy of ~1.1·R (~1.25·R at the metal sublattice and 0.95·R at the non-metal sublattice) and maintain a hardness of 36–38 GPa even when annealed at 1200 °C, contrary to compositionally simpler coatings, which soften to below 29 GPa.

These findings highlight the advantages of compositionally complex mixed ceramic coatings, which outperform simpler Ti-B-N or Ti-C-N coatings with similar structure and composition. Furthermore, they demonstrate how solubility limits can be extended beyond currently known boundaries through advanced materials science, enabling outstanding properties.

MA-ThP-8 Ab Initio Assessed Influence of Si on the Structural Integrity of Group IV Transition Metal Diborides*, Christian Gutschka, Lukas Zauner, Thomas Glechner,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; David Holec,* Department of Materials Science, Montanuniversität Leoben, Austria*; **Helmut Riedl [helmut.riedl@tuwien.ac.at]**,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal diborides, a class of refractory ceramics, have been shown to exhibit remarkable high-temperature stability and mechanical properties, encouraging research on their bulk and thin film forms. Scientific interest has been directed towards the formation of meta-stable solid solutions with silicon, with the aim of enhance oxidative properties and fracture characteristics. However, theoretical investigations of such ternary compounds remain rare. Therefore, in this study the structural, energetical, and mechanical properties of the Ti-Si-B_2, Zr-Si-B_2, and Hf-Si-B_2, as well as their vacancy dynamics, were explored with the help of Density Functional Theory (DFT). In all three systems, silicon is observed to prefer the boron sublattice. Through structural analysis, solubility limits of 24 at. %, 27 at. %, and 25 at. % of Si in $Ti(Si,B)_2$ $Zr(Si,B)_2$, and $Hf(Si,B)_2$, could be established, respectively. An analysis of simulated XRD patterns, Radial Distribution Functions (RDFs), and Crystal Orbital Hamilton Populations (COHPs), revealed that the loss of AlB_2-type symmetry could be attributed to the formation of Si clusters. Simulations of elastic properties demonstrated a reduction of Young's moduli but enhancing ductility criteria, both with increasing silicon contents, which was in line with experimental values up to 15 at. % Si. Concerning defects, the study revealed a structural instability of ternary AlB_2-type compounds with respect to metal vacancies. Furthermore, it was observed that both metal and boron vacancies showed a decreasing influence on the formation energies as the Si content increased.

MA-ThP-9 Fabrication and High-Temperature Test of Light-Weight Insulation Materials and Coatings for Reusable Thermal Protection Materials*, **Seongwon Kim [woods3@kicet.re.kr]**,* Korea Institute of Ceramic Engineering and Technology, Republic of Korea

Light-weight ceramic insulation materials and high-emissivity coatings were fabricated for reusable thermal protection systems (TPS). Alumina-silica fibers and boric acid were used to fabricate the insu¬lation, which was heat treated at 1250°C. High-emissivity coating of borosilicate glass modified with $TaSi_2$, $MoSi_2$, and SiB_6 was applied via dip-and-spray coating methods and heat-treated at 1100°C. Testing in a high-velocity oxygen fuel environment at temperatures over 1100°C for 120 seconds showed that the rigid structures withstood the flame robustly. The coating effectively infiltrated into the fibers, confirmed by scanning electron microscopy, energy-dispersive X-ray spectroscopy, and X-ray diffraction analyses. Although some oxidation of $TaSi_2$ occurred, thereby increasing the Ta_2O_5 and SiO_2 phases, no significant phase changes or performance degradation were observed. These results demonstrate the potential of these materials for reusable TPS applications in extreme thermal environments.

Author Index

Bold page numbers indicate presenter