Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-1-TuM

Coatings to Resist High-temperature Oxidation, Corrosion, and Fouling I

Moderator: Francisco Javier Pérez Trujillo, Universidad Complutense de Madrid, Spain

8:20am **MA1-1-TuM-2 Tunable Aluminide Coatings for Surface Finish and Improved Oxidation and Hot Corrosion Behaviour of Additive Manufactured Ni-Based Superalloys***, **Fernando Pedraza (fpedraza@univ-lr.fr)**, D. PIEL, T. KEPA,* La Rochelle University, France **INVITED**

The widespread use of additive manufactured (AM) components has become a hot topic over the past 10 years. Many of the mechanical properties are surface-dependent because of the derived roughness due to e.g. semi-molten powders. The reactivity of the AM materials also increases because of the greater active surface. In addition, AM materials contain many metallurgical defects including e.g. dislocations, twins, various grain sizes, etc. which make the materials more susceptible to attack in particular under high temperature conditions where the harsh gas and molten reagents can go through. While different alternatives including e.g. chemical and electrochemical polishing, laser remelting, etc. have been proposed to lower the roughness and densify the surface, the AM materials still degrade fast.

The alternative that will be presented in this paper is based on the use of aluminium-based coatings made by slurry. As opposed to electrolytic or gas phase processes where the coating follows the surface roughness, the slurry process partly melts the surface, blends the uppermost layers of the AM alloy with the coating material and results in a diffused gradient layer that can be tailored to tune the chemical composition and microstructure. The examples will be given for different additive manufactured nickel-based alloy systems including the popular equiaxed or single crystalline nickel-based superalloys.

Simple nickel aluminide coatings will be shown to dramatically improve the oxidation resistance of IN-718 at temperatures as high as 800°C and of Alloy 699XA at 950°C through the development of a thin and adherent Al_2O_3 scale. The application of Al/Si slurry coatings improves dramatically the hot corrosion resistance under Na_2SO_4 against conventional vapour phase and simple Al slurries due to the layered segregation of Si_xW_y. The incorporation of microreservoirs made of MCrAlY in the aluminium diffusion coating matrix can in contrast improve both the oxidation and the hot corrosion resistance.

9:00am **MA1-1-TuM-4 Application of Machine Learning Algorithms to Characterize Aluminide Diffusion Coatings and to Predict their Ageing Behavior***, **Vladislav Kolarik (vladislav.kolarik@ict.fraunhofer.de)**, M. Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany*; P. Praks,* IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia*; R. Praksova,* IT4Innovation National Supercomputing Center, VSB - Technical University of Ostrava, Czechia

Aluminide diffusion coatings are an efficient and economic technique to protect steels against corrosion at high temperatures in harsh environments. They can be deposited as aluminum slurry through various deposition methods, such as spraying or brushing, followed by a heat treatment to form the diffusion coating. Machine learning algorithms offer a significant potential for optimizing and customizing the coatings for a specific application with desired coating characteristics and for predicting the ageing behavior during operation. The experimental effort can be minimized reducing the costs significantly and accelerating the development. Symbolic Regression was chosen to investigate the potential of machine learning to determine the slurry deposition parameters that lead to the targeted coating characteristics and to predict the ageing behavior.

Output parameters characterizing the diffusion coating were defined as well as input parameters on which they depend. Experimental data from former projects were used to train the algorithm applying a train/cross-validation split of 50/50. To assess the robustness of the coating system the thickness of the deposited slurry was calculated top-down from the experimental data after different ageing times and plotted versus the values adjusted during the slurry deposition process. The result reveals the deviation to the adjusted values and separates the sample sets, where the deposition process was under control from those with high fluctuation of the slurry thickness deviation. Output parameter characterizing the ageing progress, such as coating thickness, number of layers and their thicknesses, pores concentrations and FeAl precipitations in the Fe_2Al_5 layer were calculated as a function of time inferring predictions. The results show that machine learning is highly useful for complex systems influenced by numerous parameters, whose interrelation and meaningfulness is difficult to be described by classical physical modelling.

9:20am **MA1-1-TuM-5 Pack-Aluminizing Mechanisms in Stainless Steel Additively Manufactured***, E. B. Varela,* PGMEC-Universidade Federal do Paraná, Brazil*; H. Abreu-Castillo,* PIPE - Universidade Federal do Paraná, Brazil*; G. Prass, J. Pacheco,* Instituto SENAI de Inovação em processamento a laser,, Brazil*; **Ana Sofia C. M. D'Oliveira (sofmat@ufpr.br)**,* Universidade Federal do Paraná, Brazil

Sustainable development of high temperature parts typically requires surface treatment to enhance performance, including metallic parts processed by additive manufacturing (AM). Challenges of diffusion processed surfaces depend on the microstructure of AM parts being protected and are being addressed in this investigation. This research contributes to the discussion of the impact of additive microstructure on the diffusion mechanisms and characteristics of aluminide coatings. Pack-aluminization was applied to AM AISI316L stainless steel processed by PTA-DED, L-DED and L-PBF. Pack-aluminizing was carried out at 850°C for 1h and with a pack-mixture composition of 10%Al-3%NH_4Cl-87%Al_2O_3. Results show that, regardless of the substrate condition, aluminized coatings are composed of an external Fe_2Al_5 intermetallic layer and an interdiffusion region exhibiting two sub-layers, an intermediate layer of the intermetallic FeAl and an internal layer of α-Fe(Al) close to the substrate. The first evidences of the impact of additive multilayer structures is the non uniform interface with the substrate associated with the interlayer regions. Changes in the microstructure in these regions regions are a consequence of solidification mechanisms of each deposited layer creating local fluctuations in the atomic diffusion rate. The substrate microstructure also impacts the thicknesses of each layer, external and interdiffusion regions of the aluminized coatings. With the thicker external layer exhibited by the roller substrate (21,5±1,3 μm) and the thicker interdiffusion layer for the Stainless steel processed by PTA-DED (3,6± 0,4 μm): It is interesting to point out that inspite of the differences in microstructure L-DED and L-PBF AM materials exhibit very similar features that differ from PTA-DED that has a thinner external, 15,7±0,9 μm of the set of materials processed. The observed differences between coatings can be accounted for by the non-uniform characteristics of microstructure of the multilayer additive materials as opposed to the more uniform grain structure of the rolled substrate. Between additive materials, the finer microstructure of L-AM materials induced a larger density of diffusion paths forming a thicker external layer ±19 μm. Results allow to conclude that thicker external layers are accompanied by a thinner interdiffusion region behavior associated with an earlier formation of two compositional gradients in the coarser PTA-DED microstructure, at the surface and at the interface between the Fe_2Al_5 /substrate, accounting for the thicker sublayers in the interdiffusion region.

9:40am **MA1-1-TuM-6 Synthesis of Novel Multi-Element TM-Aluminides by Multilayer Magnetron Sputtering***, **Vincent Ott (vincent.ott@kit.edu)**, M. Duerrschnabel, U. Jaentsch, M. Klimenkov, S. Ulrich, M. Stueber,* Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Germany

Transition metal Aluminides in the B2 structure like NiAl and FeAl are well known for their combination of mechanical properties and oxidation resistance which make them suitable materials for high temperature applications. However, these materials often suffer from brittle material behavior at room temperature, hampering their machinability and utilization. The RuAl phase shows improved RT ductility due to its greater number of available slip systems compared to other binary aluminides in the B2 structure. To investigate and potentially further improve the mechanical and protective behavior of transition metal aluminide thin films, a multi-layer approach was used to synthesize novel multi-elemental solid-solution aluminides of the type (Ru_x, Me_{1-x})Al. The deposition of nanoscale multilayer films thereby allows to circumvent thermodynamic restrictions in equilibrium bulk conditions to generate supersaturated aluminide phases in thin films outside the phase boundaries. The correlation between the thin films microstructure and the mechanical properties is discussed. The phase formation is observed by HT-in-situ-XRD, while the mechanical properties as well as the microstructure are examined by microindentation and TEM analysis respectively.

10:00am **MA1-1-TuM-7 Structural Evolution and Oxidation Resistance of Al/Si Alloyed Transition Metal Carbide Thin Films***, Sophie Richter* ***(sophie.richter@tuwien.ac.at)****,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; E. Ntemou, D. Primetzhofer,* Department of Physics and Astronomy, Uppsala University, Sweden*; T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*; J. Ramm,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; H. Riedl,* Institute of Materials Science and Technology, TU Wien, Austria

Transition metal carbides (TMCs) are known for their mechanical properties, high-temperature stability and melting points exceeding 3000 °C. However, their exceptional high-temperature properties are offset by their sensitivity to oxidation. This study focuses on an alloying strategy incorporating Al and Si as strong oxide-forming elements to extend their oxidation resistance in demanding environments. Using a combinatorial physical vapor deposition (PVD) approach, group IV to VI transition metal carbides were systematically investigated by co-sputtering Al and Si next to TMCs. This comprehensive study covers a wide range of structural and chemical compositions, which are thoroughly characterized by X-ray diffraction (XRD), nanoindentation, and elastic recoil detection analysis (ERDA) calibrated X-ray fluorescence (XRF) to achieve precise chemical quantification. Subsequently, a subset of selected compositions based on structural and mechanical criteria is analyzed concerning their oxidization resistance. In-situ XRD monitors the formation of oxide scales in synthetic air environments up to 1200 °C. In addition, conventional oxidation experiments in a box furnace contribute to a comprehensive understanding of the oxidation behavior of these TMCs. The formed scales are thoroughly described by transmission electron microscopy unraveling details on the diffusion kinetics of the oxide formers. This research not only explores the fundamental mechanisms that determine the scale formation of TMCs, but also provides valuable insights into the growth mechanism of ternary face-centered cubic (fcc) TM-Al/Si-C solid solutions synthesized by PVD techniques.

10:20am **MA1-1-TuM-8 Hot Corrosion of Arc Evaporated $Ti_{1-x}Al_xN$ on Ni-Cr-Co Based Superalloys***, O. Hudak, A. Scheiber, P. Kutrowatz, T. Wojcik,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria*; J. Ramm, O. Hunold,* Oerlikon Balzers, Oerlikon Surface Solutions AG, Liechtenstein*; S. Kolozsvári, P. Polcik,* Plansee Composite Materials GmbH, Germany*;* ***Helmut Riedl (helmut.riedl@tuwien.ac.at)****,* Christian Doppler Laboratory for Surface Engineering of high-performance Components, TU Wien, Austria

Hot corrosion is an accelerated oxidation process that occurs in high-temperature environments (650-950 °C) in the presence of sulfur-rich exhaust gases and salt-impurities. The subsequent formation of high-melting sulfate salts and their deposition on machine components induces accelerated degradation of operating parts through the formation of a porous and non-protective corrosion scale. Notably, Ni-, Co-, and Fe-base superalloys used in aerospace and power generation industry are particularly susceptible to hot-corrosion attacks.

This research explores arc-evaporated $Ti_{1-x}Al_xN$ as a promising protective coating material mitigating hot-corrosion effects on superalloys. $Ti_{1-x}Al_xN$ coatings with varying metal ratios were arc evaporated onto a NiCoCr-based superalloy and subjected to hot-corrosion testing in a specially designed hot corrosion rig. Utilizing a Na_2SO_4-$MgSO_4$ salt mixture, both coated and uncoated samples were thermally treated in an SO_x-rich atmospheres for a duration of up to 30 h. The primary objective was to enhance the understanding of the corrosion mechanisms of $Ti_{1-x}Al_xN$ coatings under low-temperature hot corrosion (LTHC, at 700°C), as well as high-temperature hot corrosion (HTHC, at 850°C) conditions. The scale formation was analyzed through a variety of high-resolution characterization techniques ranging form XRD, SEM, to HR-TEM.

Results revealed that arc evaporated Ti_{1-x}AlxN exhibits superior corrosion resistance compared to the bare NiCoCr-based alloy in both temperature regimes. Under LTHC conditions, a localized and accelerated attack was observed, driven by an initial nitride-to-sulfate transformation and followed by a synergistic fluxing mechanism. This mechanism involved the formation of layered oxide domains rich in TiO_2 and Al_2O_3, due to the acidic nature of the liquid salt interface. The obtained scale was dominated by Al_2O_3, known for its enhanced stability under acidic conditions. In contrast, under HTHC conditions, a more uniform development of the corrosion scale was noted. Similar to LTHC, a sequential fluxing produced Ti-rich and Al-rich oxide domains that over time formed a layered corrosion scale. The stability of TiO_2 under basic conditions resulted in the primary formation of a porous TiO_2 scale at the scale-salt interface, followed by a substantial band of Al-rich oxide.

This research contributes valuable insights into the hot corrosion behavior of arc evaporated $Ti_{1-x}Al_xN$ coatings, and highlights their potential as protective coatings for components exposed to aggressive high-temperature environments.

10:40am **MA1-1-TuM-9 Characterization of Li-rich Corrosion Products Formed onto Aluminized and Uncoated Steels after Molten Carbonates Exposure***, P. Audigié, S. Rodríguez,* ***Alina Agüero (agueroba@inta.es)****,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Public authorities are strongly encouraging the adoption of new thermal energy storage (TES) systems in order to meet the requirements for clean energy worldwide. However, installation, maintenance and materials for such TES imply rather high costs which can hinder their implementation. To remedy this, various corrosion resistance slurry aluminide coatings have been developed at INTA onto ferritic and austenitic steels as low-cost alternative materials for structural components in contact with molten salt. Emphasis has been placed on Li-rich molten carbonate exposure at high temperature of such coated and uncoated materials and expressly on the identification and characterization by advanced techniques (GDOES, TEM) of Li-rich corrosion products as Li cannot be detected by conventional techniques. Microstructural features of $LiFeO_2$, $LiFe_5O_8$, $LiAlO_2$ both alpha- and gamma- phases among others and Li effect will be discussed. Presence of two distinct peaks of Li were detected in the $LiAlO_2$ oxide formed onto the slurry aluminide coated T92 heat treated at low temperature and exposed 2000h at 650ºC with Li, Na and K carbonates. Similar behavior was observed with the aluminized 310H austenitic steel after 1000h of exposure in the same environment at 700ºC. Li penetration into the different studied materials will thus be described.

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