Protective and High-temperature Coatings
Room Town & Country A - Session MA1-1-TuM

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

Moderators: Dr. Justyna Kulczyk-Malecka, Manchester Metropolitan University, UK, **Prof. Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

8:00am **MA1-1-TuM-1 High Temperature Corrosion Resistant Coatings: Recent Aluminide Developments for Renewable Energy Applications***, **Pauline Audigié [audigiep@inta.es]**, Cristina Lorente, Sergio Rodriguez, Loïc Oger, Alina Agüero,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain **INVITED**

Protective coatings are known for many decades as first-rate mitigation methods to hinder high-temperature oxidation and corrosion in several industrial sectors. For many years, INTA has been developing diffusion coatings by spraying Al slurry onto different substrates such as different composition of Fe, Ni, Ti and Mo-based alloys. Recently, new developments have been focused on renewables energies including concentrated solar power (CSP) plants with thermal energy storage systems and hydrogen-fueled combustion systems. For those applications, some components require coatings that are resistant to corrosion/oxidation and mechanical stresses which might also give rise to considerable cost reduction by using lower cost alloys. In particular, new slurry aluminide coatings deposited onto TA6V and Ti6246 Ti-based alloys are being explored for compressor parts of aircraft engines and also onto 310H and 347H austenitic steels for molten nitrate and carbonate resistance in hot storage tanks and tubes in CSP plants. An overview of the global deposition process including surface preparation, deposition methods and thermal treatments will be shown for each generated coating. The coating formation mechanism and their prevailing protection mechanism in their respective corrosive environment will be presented. Furthermore, the loss of the protective oxide former element, Al in this case, by coating-substrate interdiffusion during exposure at high temperature can lead to premature degradation of the coating. Efforts have thus been pursued to reduce interdiffusion in the Ti6246 and 310H coated systems by incorporating Si particles in the slurry. This led to the formation of Si-Al rich diffusion barriers for which the latest progresses and corrosion results in both environments will be presented.

8:40am **MA1-1-TuM-3 Molten Salt Corrosion and Stress Corrosion Cracking Performance of Slurry Aluminide Coated Steels for Thermal Energy Storage***, **Loïc OGER [loge@inta.es]**, Pauline Audigié,* Instituto Nacional de Técnica Aeroespacial (INTA), Spain

Thermal energy storage systems associated to concentrated solar power (CSP) plants emerged as key technologies to allow consistent energy distribution while reducing electricity cost. However, their wide-range deployment is limited by the cost of the structural materials and by their short lifespan which imposes recurrent and expensive operation and maintenance. This is mainly due to the use of corrosive high-temperature molten salts as heat transfer fluid and to stresses generated by temperature variations. The European project COMETES was thus designed to develop coated materials as cost-effective alternatives suitable in current plants and in more aggressive operating conditions considered for next-gen CSP. The present study focused on molten salt corrosion and stress corrosion cracking (SCC) resistance of:

(1)A slurry aluminide coated P91 martensitic-ferritic steel considered as a promising alternative for current use in Solar Salt (60wt%$NaNO_3$ – 40wt%KNO_3) up to 580 ºC because of its 3 to 10 times lower cost than the currently used Ni-based materials.

(2)a newly developed coated 347H austenitic steel, capable to withstand higher operating temperatures – 700 ºC in the present study – with 32wt%Li_2CO3 – 33wt%Na_2CO_3 – 35wt%K_2CO_3 carbonate to achieve higher plant efficiency and increase the heat storage duration.

1000 h-hot corrosion study of the uncoated materials in their respective molten salt and temperature showed significant degradation of the substrates with the formation of various alkaline oxides. Tensile tests performed at a strain rate of 10^{-3} s^{-1} after such exposure showed a relatively low sensitivity of the P91 to SCC while a collapse of the 347H mechanical properties was evidenced. The slurry aluminide coated P91, composed by a homogeneous FeAl outer layer with Kirkendall pores formed in the interdiffusion zone, significantly increased the corrosion resistance when compared with the uncoated P91 in Solar Salt capable to withstand up to 10,000 h at 580 ºC. On the 347H, a 3-layers coating developed with several Fe-Al-Cr rich phases in the top layer. Despite the hardness heterogeneity (200 to 1000 $HV_{0.05}$) and the coating evolution along the exposure with the occurrence of phase transformations and Cr_3Si precipitation, aluminide coated 347H withstood at least 2,500 h in carbonatesat 700 ºC with the formation of a mixed γ/α-$LiAlO_2$ top layer. From the mechanical view, both steels were shown to have slightly lower maximal stresses after coating, which was attributed to crack initiation in the latter and then propagation into the substrate. Nonetheless both coatings efficiently increased the SCC resistance of the steels in molten salts.

9:00am **MA1-1-TuM-4 Prediction of the Ageing Behavior of Diffusion Aluminide Coatings Using Machine Learning***, **Vladislav Kolarik [vladislav.kolarik@ict.fraunhofer.de]**, Maria del Mar Juez Lorenzo,* Fraunhofer Institute for Chemical Technology ICT, Germany*; Pavel Praks, Ranata Praksová,* IT4Innovations National Supercomputing Center, VSB - Technical University of Ostrava, Czechia

Aluminide diffusion coatings provide an effective and cost-efficient solution for protecting steels from high-temperature corrosion in harsh environments. They can be applied as aluminum slurries through various deposition techniques, such as spraying or brushing, followed by heat treatment to create the diffusion layer. Machine learning algorithms show great potential for modeling and predicting the aging behavior of these coatings, while facilitating their optimization and customization. Machine learning relies solely on data and does not require physical models to describe dependencies. This is especially advantageous for systems influenced by multiple parameters, where the extent of each parameter's impact on the system is not well known. Symbolic regression and decision tree-based algorithms, such as XGBoost and Catboost were employed to explore the potential of machine learning in modelling the coating characteristic over time and forecasting the ageing behavior.

Data files for input were created collecting parameters, such as time, temperature, atmosphere, overall coating thickness, thicknesses of the partial layers, number of the partial layers, type of slurry etc. To evaluate the aging process, two key output parameters were modeled based on selected input variables: (1) the ratio of the outer Fe_3Al layer to the total coating thickness, and (2) the aluminum concentration within the outer Fe_3Al layer. The first parameter indicates the conditions under which the diffusion coating evolves into a single aluminum-poor layer—this occurs when the ratio equals 1. The aluminum concentration, on the other hand, reflects how much aluminum remains in the coating, which is essential for forming a protective alumina layer. Decision tree-based algorithms, such as XGBoost, are well-suited for assessing the degree of influence of individual parameters, with time emerging as the most significant factor, followed by the thickness of the aluminum-poor Fe_3Al layer.

The results demonstrate that machine learning is highly effective for analyzing complex material systems influenced by numerous parameters, where the relationships and significance of these parameters are challenging to capture through traditional physical modeling.

9:20am **MA1-1-TuM-5 AI-Enhanced Correlative Microscopy: A Multi-Modal Approach to Automotive Coating Evaluation***, **Hugues G. Francois-Saint-Cyr [hugues.fsc@thermofisher.com]**,* Thermo Fisher Scientific, USA*; Alice Scarpellini, Bartlomiej Winiarski,* Thermo Fisher Scientific, Netherlands*; Roger Maddalena, Rengarajan Pelapur,* Thermo Fisher Scientific, USA

The automotive industry extensively employs zinc-based coatings to enhance corrosion resistance and extend the lifespan of steel components exposed to harsh atmospheric conditions. These protective layers, applied through hot-dip galvanizing and electroplating, prevent oxidation of the underlying steel. The effectiveness of these coatings depends on thorough material quality assessment, adhesion evaluation, and stringent final product control.

Scanning electron microscopy (SEM), along with other advanced analytical characterization techniques, is crucial for detailed evaluation of zinc-based coatings. SEM supports correlative microscopy (CM) workflows, integrating imaging, analytical solutions, and AI-assisted image analysis to provide a multi-modal and multi-dimensional view of the materials under investigation. The site-specific use of Plasma Focused Ion Beam-SEM (PFIB-SEM) cross-sections enables highly targeted analysis, revealing detailed microstructural features and providing comprehensive compositional and crystallographic information.

The Apreo ChemiSEM exemplifies this approach by enabling comprehensive surface and cross-sectional analysis of both coatings and steel substrates. Its correlative capabilities combine imaging, energy dispersive X-ray spectroscopy (EDS) via ChemiSEM Technology, and electron backscatter diffraction (EBSD) with the TruePix detector. Cross-sectional analysis is performed on both metallographically prepared sections and PFIB-prepared cross-sections, providing detailed insights and accelerating the characterization of coating morphology and defect identification.

Integrating imaging with ChemiSEM Technology allows for detailed investigation of surface oxidation, inclusions, and inhibition layers within the coatings. The TruePix detector identifies areas of high dislocation density and other crystalline defects, offering a deeper understanding of material weaknesses that may correlate with reduced adhesion or other issues.

AI-assisted image analysis enhances the characterization process by significantly reducing the time required to interpret complex datasets. Deep learning models integrated into the workflow provide accurate, large-scale analysis of data collected at both micro- and nanoscale levels, enabling validation over millimeter-scale regions. This synergy between advanced microscopy and AI ensures a robust and comprehensive evaluation of zinc-based coatings, linking structure, processing, property, and performance in automotive applications.

9:40am **MA1-1-TuM-6 High-Temperature Corrosion in Contact with Molten Glass Improved by Thermal Spray Coating**, ***Michelle Hartbauer* [michelle.hartbauer@uni-bayreuth.de]**, University of Bayreuth, Germany; *Thomas Dörflinger,* Neue Materialien Bayreuth GmbH, Germany; *Helge Schumann,* Wiegand-Glashüttenwerke GmbH, Germany; *Gilvan Barroso,* Rauschert Heinersdorf-Pressig GmbH, Germany; *Haneen Daoud,* Neue Materialien Bayreuth GmbH, Germany; *Florian Scherm, Uwe Glatzel,* University of Bayreuth, Germany

Glass manufacturing demands extreme conditions, exposing components to high-temperature corrosion through contact with molten glass at temperatures above 1100 °C. Thermal spray processes have emerged as a valuable solution for creating protective coatings that can significantly enhance material performance in such harsh environments. These coatings improve component longevity by increasing hardness, wear resistance, and corrosion resistance. Known for their performance, ease of application, and cost-effectiveness, thermal spray coatings are widely used across various applications.

To address these challenges, this study employs thermal spray processes to deposit an Al-Ni alloy onto a substrate of lamellar grey cast iron. Al and Ni wires are applied simultaneously via arc spray process. An electric arc generated between two consumable wires produces intense heat, melting the wire tips. Nitrogen gas then propels the molten material onto the substrate's surface, where it rapidly solidifies to form the protective coating. Heat treatment was then carried out.

To examine the coating's corrosion resistance, samples were immersed in molten glass for up to 48 h and subsequently prepared for analysis using metallographic procedures. Cross-sectional imaging allowed the analysis of the reaction zone between the thermal spray coating and molten glass.

Analyses of microstructure and chemical composition were conducted using SEM and energy-dispersive spectroscopy (EDS) across various stages: after thermal spraying, post-heat treatment, and after glass contact. Additionally, phase identification was carried out using X-ray diffraction (XRD).

Coating thicknesses with 100 - 300 µm were achieved. The differences in composition and heat treatment have a great influence on the microstructure of the thermal sprayed coatings. Differences in elemental distribution, phases formed, and their corresponding properties, particularly hardness, were observed.

10:00am **MA1-1-TuM-7 Microstructural Characterization and Isothermal Oxidation Behavior of a Nanolaminate Ti_2AlC MAX Phase Coating on TiAl 48-2-2**, ***Radosław Swadźba* [radoslaw.swadzba@git.lukasiewicz.gov.pl]**, Łukasiewicz Research Network – Uppersilesian Institute of Technology, Poland; *Bogusław Mendala, Lucjan Swadźba,* Silesian University of Technology, Poland; *Nadine Laska,* German Aerospace Center (DLR), Germany; *Sarra Boubtane,* German Aerospace Center, Germany; *Dariusz Garbiec,* Łukasiewicz Research Network – Poznań Institute of Technology, Poland

This study investigates the application of the Closed Hollow Cathode Physical Vapor Deposition (CHC-PVD) method for depositing Ti_2AlC MAX phase nanolaminate coatings on a TiAl 48-2-2 alloy substrate. During deposition, samples were placed within an 80 mm-diameter, 160 mm-long hollow cathode using a target composition of Ti-25Al-25C (at.%). The resulting coatings, approximately 12 µm thick, exhibited a columnar microstructure. Advanced characterization techniques, including High-Resolution Scanning Transmission Electron Microscopy (STEM) and High-Resolution TEM (HRTEM), were employed to analyze the microstructure of both as-deposited coatings and coatings subjected to isothermal oxidation testing.

The oxidation resistance of the obtained coatings was evaluated using Thermogravimetric Analysis (TGA) at 850 °C for 20 hours in an air atmosphere. Mass change analysis revealed that the parabolic rate constant for the coated material was over five times lower than that of the uncoated substrate. Detailed STEM and HRTEM analyses showed Ti_2AlC nanolaminates within the columnar structures, with basal planes of the Ti_2AlC phase aligned parallel to the growth direction at the core and tilted in sub-columnar regions.

After the isothermal oxidation test it was found that a very thin and continuous alumina oxide scale is formed on the coated TiAl 48-2-2 with a thickness of around 320 nm. HRTEM and FFT (Fast Fourier Transform) imaging were applied to study the phase composition of the oxide scale and showed the presence of a mixture of transition θ-Al_2O_3 and stable α-Al_2O_3.

10:20am **MA1-1-TuM-8 Harnessing Ti_2AlN MAX Phase Based PVD Coatings on Titanium Aluminide Alloys for High Temperature Applications**, ***Sarra Boubtane* [sarra.boubtanepzammouri@dlr.de]**, German Aerospace Center, Germany

Nanolaminate coatings based on MAX phases (where M= Ti, A=Al, and X is nitrogen) exhibit a distinctive combination of ceramic and metallic material properties, offering considerable potential for utilization in high-temperature environments.

It is unfortunate that the application of MAX phases as coating material on various Ti- or Ni-based alloys results in degradation due to interdiffusion processes between the coating and the alloy, which is accompanied by an Al-depletion. A promising strategy involves combining a γ-TiAl substrate with a MAX phase coating, as the substrate can serve as an Al reservoir, replenishing the coating through outward diffusion of Al. This approach could also enhance the mechanical properties of such coated components compared to other protective but brittle intermetallic coatings on TiAl alloys.

In this study, a Ti_2AlN-MAX phase-based coating was deposited using reactive magnetron sputtering using pure elemental targets of Ti, Al and nitrogen as a reactive gas. The deposition process was studied using a variety of substrates, including inert Al_2O_3 and MgO substrates, as well as an already been used γ-TiAl alloy. This alloy TiAl48-2-2 (48Ti–48Al–2Nb–2Cr in at.%), supplied by GfE–Gesellschaft für Elektrometallurgie in Nuremberg, Germany, was utilized for all oxidation and interdiffusion experiments. The two-fold rotation ensures homogeneous deposition, with a thickness of 10 µm and near to the requisite stoichiometric composition of the Ti_2AlN MAX phase. Due to the low substrate temperature during deposition, the resulting layer was X-ray amorphous. A post-annealing treatment was performed at 800°C in a high vacuum furnace for one hour for crystallization. Additionally, high-temperature X-ray diffraction (HT-XRD) in a vacuum atmosphere was conducted from room temperature to 1000°C to observe in-situ the phase formation in the Ti_2AlN coating.

Following the production of Ti_2AlN MAX Phase, a series of oxidation tests are conducted to assess the coating's performance. These include isothermal oxidation for 10 hours at 850°C in laboratory air. Hereby, the Ti_2AlN MAX phase based coating develop a thermally grown layer of predominantly alumina, which is suitable as protection in high temperature environments. Below the alumina layer the Ti_2AlN MAX phase as well as the intermetallic Al-rich phase.

Analysis techniques included GD-OES for chemical composition, XRD for phase analysis, and SEM/EDS and TEM for structural evaluation are used.

10:40am **MA1-1-TuM-9 Empowering Pvd for Corrosion Protection: Ti(Al,Mg)Gdn Coatings with Game-Changing Corrosion Performance**, ***Holger Hoche* [holger_claus.hoche@tu-darmstadt.de]**, Grafenstraße 2, Germany

Today, PVD technology is not the first choice for surface functionalization under corrosive conditions. The state-of-the-art for corrosion protection involves multilayers of electroplating or chemical corrosion protection layers, followed by a PVD top layer. This negatively affects sustainability and economic factors.

The authors successfully developed PVD-TiMgGdN and TiAlMgGdN coatings, sputtered with powder metallurgical targets in an industrial DC-magnetron PVD unit. With only a 5 µm coating thickness, corrosive mild steel substrates can be protected for at least 1000 hours in the salt spray test against corrosion [1]. By partially substituting magnesium with aluminum, the corrosion properties and manufacturability were further improved. Additionally, TiAlMgGdN coatings exhibit excellent corrosion behavior in alkaline (pH 8.5) and acidic (pH 5) environments.

This improvement is based on the synergistic effects of magnesium and gadolinium: Magnesium lowers the free corrosion potential of the coating, thereby reducing the susceptibility to galvanic corrosion. Gadolinium enhances the hydrophobicity of the surface, affects the conductivity, and supports the formation of stable passivation layers [2].

The influence of Gd, Mg, and Al on the corrosion protection performance will be investigated. Therefore, coatings with different Al/Mg proportions and varying Gd content were produced and compared regarding their microstructural, chemical, physical, and corrosion properties. Corrosion properties were investigated using different corrosion tests. The coating surfaces were also analyzed by nanoindentation measurements and chemical analysis to gather knowledge about the coating stability during corrosive stress.

The key properties influencing the corrosion protection effect of Ti(Al, Mg)Gd will be evaluated. Additionally, the effect of the specific chemical composition on the coating properties will be investigated. Understanding the key properties and their correlation with chemical composition allows for the specific design of functional corrosion-resistant PVD coatings.

[1] T. Ulrich, C. Pusch, H. Hoche, P. Polcik, M. Oechsner, Surface and Coatings Technology 422 (2021) 127496.

[2] H. Hoche, T. Ulrich, P. Kaestner, M. Oechsner, Vakuum in Forschung und Praxis 36, 2 (2024) 40.

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