Protective and High-temperature Coatings
Room Palm 1-2 - Session MA1-3-WeM

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

Moderators: Vladislav Kolarik, Fraunhofer Institute for Chemical Technology ICT, Germany, **Francisco Javier Pérez Trujillo**, Universidad Complutense de Madrid, Spain

8:00am **MA1-3-WeM-1 Characterization and Evaluation of Physical-Chemical Properties of Novel Ternary and Quaternary Molten Salts and Their Economic and Environmental Impact in Parabolic Trough Technology: Corrosion Effects**, *M. Lambrecht, D. Maria Teresa, L. Maria Isabel, G. Garcia Martin, J. Chaves,* ***Francisco Pérez Trujillo (fjperez@ucm.es)***, Universidad Complutense de Madrid, Spain; *P. Audigie, A. Aguero,* INTA, Spain

Only molten salt combinations are used as a heat storage medium in CSP to date. Alkaline nitrates and nitrites have been successfully utilized as heat transfer fluids (HTF) and heat storage medium (HSM) in concentrated solar power (CSP) plants. Particularly, the binary mixture combination 60%$NaNO_3$ - 40%KNO_3, well known as Solar Salt with a freezing point around 220ºC and thermal decomposition at 560ºC [1]. Separately, there is a synthetic thermal oil that comprises the commercial parabolic trough (PT) technology to capture the heat of solar radiation. This costly HTF with a melting point about 12ºC and high environmental impact yields the heat to Solar Salt by means of exchangers. The maximum thermal energy storage temperature reached is about 390ºC, their energy power is thus limited by the organic heat carrier fluid. There are investigations aiming to increase the working temperature range a long with a unique molten salt (MS) as heat capture and storage medium. Ternary and quaternary low melting point mixtures with addition of $LiNO_3$ and $Ca(NO_3)_2$ have been presented as direct systems candidates according to their better physic - chemical properties than Solar Salt but, nonetheless, these previous investigations have deemed a full properties study with additional environmental and economic aspects to weigh the best selection criterion to envisage alternative fluids.

This investigation evaluates the important properties (melting point, degradation temperature, specific heat capacity, density and energy density) of the novel mixtures46% wt.$NaNO_3$-19%wt.$Ca(NO_3)_2$- - 35%wt.$LiNO_3$ (T1) and 33%wt.$NaNO_3$-22%wt.KNO_3-29%wtCawt.$(NO_3)_2$-16% wt.$LiNO_3$ (Q-1). Life Cycle Assessment (LCA) has been used to calculate the environmental impact of the mixtures through the software tool Simapro7 in comparison with the Solar Salt. Likewise, an economic simulation of their usage in a direct and indirect parabolic through (PT) configuration has also been estimated by means of Levelised Cost of Energy (LCOE) parameter, which was customized for the TES facility, ($LCOE_{TES}$).

The effects of molten salts chemical composition in the high temperature corrosion of metalic materials and coatings will be analized.

In this study, a 50 MW and 6 hours heat storage capacity PT plant has been considered for $LCOE_{TES}$ estimation . This parameter was assessed by means of an in-house method from articles references and data extrapolation to simulate price variations by replacing novel multicomponent fluids by Solar Salt as HSM.

8:20am **MA1-3-WeM-2 Influence of the BN Content on the Microstructure and the Mechanical Properties of Cr_3C_2-NiCr-BN Composite Coatings Prepared by a Novel HVOF Process Using Ethanol as a Fuel**, *S. Liu,* UTBM, France; *M. Arab Pour Yazdi,* ***Pavel Sedmak (pavel.sedmak@anton-paar.com)***, *J. Nohava,* Anton Paar, Switzerland; *M. Moliere, H. Liao,* UTBM, France

Cr_3C_2-NiCr-BN composite coatings were thermal sprayed on 304 stainless steel substrates using an ethanol-fueled High-Velocity Oxygen Fuel (HVOF) process. We examined the impact of varying Boron Nitride (BN) contents (ranging from 0 wt% to 15 wt%) in the feedstock on the microstructure and mechanical properties of the resulting coatings. Our findings reveal that the different BN contents significantly influence the microstructure, interlayer porosity, nanohardness, scratch resistance, and sliding wear resistance of the composite coatings. As the BN content increased, the interlayer porosity of the coatings increased and the BN content also contributed to an increase in the nanohardness of the films.In addition, a higher BN content resulted in a reduction in the coefficient of friction, but at the expense of an increase in the wear rate and a decrease in the scratch resistance. Notably, when the BN content reached 15%, the composite coating exhibited its lowest coefficient of friction. However, the wear rate was simultaneously increased due to the higher interlayer porosity of this particular coating. These results provide valuable insight into the optimization of BN content to achieve the desired balance of mechanical properties in Cr_3C_2-NiCr-BN composite coatings.

8:40am **MA1-3-WeM-3 Oxidation Behavior of Si-Based Coatings on Refractory Multi-Principal Element Alloys**, ***Brady Bresnahan (bresn047@umn.edu)***, *D. Poerschke,* University of Minnesota, USA

The large design space for refractory multi-principal element alloys (MPEAs) provides opportunities to tune alloy chemistry to simultaneously optimize the bulk and surface properties. This investigation studied Si-based coatings to improve the oxidation resistance of refractory alloys. A set of MPEAs systematically exploring composition variables related to silicide formation were produced by arc melting and coated by pack cementation and slurry processing. The effects of alloy and coating compositions on coating microstructure were studied to understand refractory metal partitioning between silicide phases. The phase evolution after oxidation was similarly explored where the tendency to form protective oxides and mass change were used to evaluate the composite material performance and understand alloy and coating composition effects. These insights will enable coupled alloy and process design to improve oxidation resistance while taking advantage of the superior high temperature yield strengths of refractory MPEAs for aerospace applications.

9:00am **MA1-3-WeM-4 Multifunctional Nanostructured ZrN-Cu Coating for Maritime Applications**, ***José D. Castro (jodcastroca@unal.edu.co)***, University of Coimbra, Portugal; *M. Lima, I. Carvalho,* University of Minho, Portugal; *J. Sánchez-López,* Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain; *R. Escobar-Galindo,* University of Sevilla, Spain; *C. Rojas,* Instituto de Ciencia de Materiales de Sevilla (ICMS), Spain; *S. Carvalho,* University of Coimbra, Portugal

Ships are essential to globalisation since they are the primary mode of transportation for goods worldwide. Any potential ship issue could affect the global economy. Corrosion and biofouling are prevalent problems linked to maritime elements. From this angle, the most widely used product was paint made of tributyltin (TBT), which was outlawed in 2008. Given this requirement, multifunctional coatings appear to be a great alternative to TBT. Magnetron sputtering technology can obtain nanoarchitectures to gather different materials and enhance characteristics. The present work presents an insight into a nanostructured film with ZrN and Cu (obtained via Deep Oscillation and DC magnetron sputtering, respectively). SS316L was used as the substrate, widely used in the naval industry. ZrN coating without copper was employed as a control sample. SEM, EDS, XRD, TEM, Nano-indentation, scratch tests, and tribology measurements assessed the characteristics of the films. Electrochemical impedance spectroscopy (EIS) until 30 days and potentiodynamic polarisation measurements were conducted in a 3.5 wt. % NaCl solution to replicate the work regime. The halo test evaluated the inhibition of microorganisms. The results demonstrate that Cu migration towards the surface (with chemical activation using NaOCl solution) reduces bacterial growth. Besides, inductively coupled plasma optical emission spectrometry (ICP-OES) and transmission electron microscopy (TEM) show that the ZrN nanolayers (~ 6nm thick) control the embedded copper nanoparticles (~ 12 nm thick) release. On the other hand, the chemical activation decreases the film corrosion resistance, the mechanical properties and the tribological performance regardless of the testing conditions (wet or dry). The findings indicate that the obtained films may be used instead of TBT paint in components used in ships as a potential way to prevent biofouling and corrosion when exposed to seawater.

9:20am **MA1-3-WeM-5 New Black Ceramic Coating on LZ91 Magnesium Alloys by Micro-Arc Oxidation**, ***Hung-Chi Chen (mouyuan75@yahoo.com.tw)***, *S. Jian,* Ming Chi University of Technology, Taiwan

LZ91 Magnesium alloy has improved mechanical properties and a low density but their limited resistance to corrosion limits their application. Therefore, it is a great challenge to increase the stability of LZ91 alloys under corrosive factors and environments. The anodized oxide film of magnesium alloy has many defects (poor bonding strength, low wear and corrosion resistance,) in traditional surface coloring technology. These defects have largely limited the applications of magnesium alloy. Micro-arc oxidation (MAO) is a new electrochemical surface treatment technology, suitable for treating the aluminum, magnesium and titanium and other light metal alloys. In electrolyte by the arc discharge plasma generated of

the substrate oxidation and high temperature melting, the film was formed with high hardness and corrosion resistance.

This study uses MAO treatment to increase the corrosion resistance of LZ91 alloy, used copper oxide and $KMnO_4$ to change MAO film color. Then, black ceramic film with uniform color, smooth surface, compact structure and excellent corrosion on LZ91 alloys was successfully obtained by MAO treatment. The aim of this study is to added with various chemical element in MAO electrolyte to change the film color to black and has excellent corrosion resistance.The morphology, structure, adhesion and corrosion behavior of the bi-layered composite coating has been investigated by scanning electron microscopy (SEM), 3D white light interferometry. In this study, MAO coatings were prepared, and the effects of adding $KMnO_4$ and copper oxide to the electrolyte on the corrosion resistance and color of the coating LZ91 magnesium alloy were evaluated.

11:00am **MA1-3-WeM-10 Study on the Characterization of Adding CeO_2 Particles on Micro-arc Oxidation Coated AZ91D Magnesium Alloys***, **Po-Wei Lien (lanbow888@gmail.com)**,* MING Chi University of Technology, Taiwan

AZ91D magnesium alloy has the advantages of low density, high tensile strength, high elongation, and easy processing. Compared with other light metals, magnesium alloys are lighter. And it has been widely used in our daily life. Unfortunately, aluminum-magnesium alloys are prone to corrosion, which may cause serious consequences, so a simple and environmentally friendly surface treatment technology must be developed.

Micro-arc oxidation (MAO), also known as plasma electrolytic oxidation, is one of the most effective and emerging methods for forming inorganic ceramic layers on various light metals. Compared to the traditional anodizing process, MAO coatings exhibit higher mechanical properties, enhanced corrosion resistance, and are also more environmentally friendly. During the MAO treatment, due to the deposition effect, the coating solidifies and contracts, resulting in surface structural defects such as microcracks. Hence, the addition of CeO_2 particles in the electrolyte aims to seal micro-pores and introduce self-healing capabilities.

This study uses AZ91Dwas utilized as the research substrate, and CeO_2 was introduced into the electrolyte. The investigation aimed to observe the presence of CeO_2 particles within the micro-pores on the MAO surface and evaluate the self-healing functionality during salt spray experiments. Surface corrosion resistance of AZ91D was examined through scanning electron microscopy (SEM) to assess its microstructure. Corrosion identification was conducted via electrochemical impedance spectroscopy (EIS) and salt spray testing. Surface roughness was measured using atomic force microscopy (AFM).

Keywords: AZ91D alloy; Ceramic oxide layer ; Micro-arc oxidation; CeO_2 particles ; self healing

11:20am **MA1-3-WeM-11 Characteristics Of High-temperature Resistant Coating Prepared By the Liquid Spray Technique***, **Yan-Rui Chen (eric19990329@gmail.com)**,* National Taipei University of Technology, Taiwan*; T. Wu,* Researcher of National Chung-Shan Institute of Science & Technology, Taoyuan city, Taiwan*; Y. Yang,* Distinguished professor of National Taipei University of Technology, Taiwan*; Y. Wu,* Professor of National Taipei University of Technology, Taiwan

In the coating technology, liquid spray (LS) is different from the traditional thermal spraying technology. The liquid spray coating is made by using compressed air. The spray liquid sprayed from the nozzle is subjected to high pressure and collides with the still air at high speed. The liquid spray splits and slows down due to air resistance, and turns into mist to form a coating,which can keep the original characteristics of the material during the spraying process and have a denser coating. Refractory metals, boride (XB_2), has good performance at high temperature, used in the electronics industry, aviation and defense. This study used liquid spray to prepare refractory metals boride (XB_2),high temperature resistant coating, discusses the liquid spray under different process parameters (working distance, solidification conditions) affected the microstructure changes of the coating and its mechanical properties, such as porosity, hardness, tensile strength, etc.

11:40am **MA1-3-WeM-12 Development of Tantalum Bond Coating for Thermal Barrier Coating by the Cold Spray***, **Wei-Che Hung (xauxdy111@gmail.com)**,* National Taipei University of Technology, Taiwan*; W. Li, Y. Chung,* Researcher of National Chung-Shan Institute of Science & Technology, Taiwan*; Y. Yang, Y. Wu,* National Taipei University of Technology, Taiwan

In the coating technology, cold spray(CS) is different from the traditional thermal spraying technology. The cold spray coating is formed by plastic deformation without high temperature melting, which can keep the original characteristics of the material during the spraying process and have a denser coating. This study we focus on depositing tantalum(Ta) as the protective coating and also the bond coat for the thermal barrier coatingon differentcurvature shape to simulate curved shell of an actual aircraft by using cold spray process.The results show that the cold spray coating can cause the powder to have good plastic deformation as the chamber pressure, temperature and closer working distance increase, so it has lower porosity and forms a dense coating. The Ta bond coat is well bonded with the substrate and atmospheric plasma spraying is used to prepare the YSZ top coat.

12:00pm **MA1-3-WeM-13 Protection Against Heavy Oil Fouling and Sulfidation: Comparison of PVD and Thermal Sprayed Coatings***, **Fellipy Rocha (fellipy.rocha@polymtl.ca)**,* Polytechnique Montréal, Canada*; L. Vernhes, F. Khelfaoui,* Velan, Canada*; G. Patience, J. Klemberg-Sapieha, L. Martinu,* Polytechnique Montréal, Canada

Valve malfunctions pose a significant and expensive threat to the gas and oil industry, leading to valve position switch failure,poor reactor pressure control, and shutdown. Safety and environmental adverse phenomena are related to worn valve maintenance. The valves are subjected to severe service at high temperature (300 – 450 °C), high pressure drop (20 – 250 bar), and erosive reactor effluents. Heavy crude oil and bitumen hydrocracking require materials that simultaneously withstand wear, oxidation, sulfidation, and coke deposition. In this work, we evaluate the protective efficacy between thin magnetron sputtered films and thermally sprayed Co-based coatings. The samples were submerged in sour crude oil at 450 °C and 110 bar for 2 h to assess their fouling resistance.

In the first part, we evaluated three thermal sprayed Co-based coatings, Co-1, Co-2, and Co-3, varying mostly in Ni, Mo, Si, W, and C contents. The as-sprayed samples exhibited typical lamellae structure, and after fusing they presented an enhanced crystallinity with a Co-Cr-Mo-Si microstructure. Surface image analysis allowed us to quantify the level of surface fouling; specifically, the worst-performing Co-1 coating showed 100% intensity, followed by 89%, and 75% for Co-2 and Co-3. After heat treatment, the same samples exhibited 95%, 15%, and 3% intensity, respectively. SEM-EDS/WDS images confirmed sulfur infiltration into the defects of the as-deposited coatings, as well as a better performance against sulfidation after fusing.

In the second part, we studied room temperature sputtered Al_2O_3 that was initially amorphous with a hardness of 11.1 GPa. Annealing at 1000 °C formed different metastable alumina polymorphs, predominantly γ-Al_2O_3 and α-Al_2O_3. Heat treatment improved alumina adhesion and increased hardness to 20.6 GPa. FIB-SEM-EDS cross-section analyses revealed an interaction between the substrate and the annealed coating. No fouling was observed on the amorphous Al_2O_3, but it was noted on the annealed samples. For comparison, HiPIMS-deposited nitride coatings fabricated with a cylindrical magnetron exhibited a very good adhesion and higher hardness, as well as good fouling protection.

In conclusion, we developed and successfully applied an optical technique to assess fouling on different surfaces. In general, amorphous materials tend to perform better, and especially coatings possessing high hardness are adequate for the heavy oil erosive environment.

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