# Tuesday Morning, May 23, 2023

## Coatings for Use at High Temperatures
## Room Pacific E - Session A1-3-TuM

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

**Moderators: Gustavo García-Martín**, REP-Energy Solutions, Spain, **Dr. Justyna Kulczyk-Malecka**, Manchester Metropolitan University, UK

8:00am **A1-3-TuM-1 Excellent Tribological, Mechanical, and Anti-Corrosion Performance of Agro-Waste as Corrosion Inhibitor for Carbon Steelin an Acidic Environment***, **Omotayo Sanni**, J. Ren, T. Jen,* Department of Mechanical Engineering Science, University of Johannesburg, South Africa

Presently, in the field of corrosion, the main goal is to develop environment-friendly and effective corrosion inhibitors that can be utilized to substitute conventional corrosion inhibitors, which are toxic. Therefore, the present work aims to investigate the microstructures, mechanical, corrosion, and tribological performances of agro-waste as a potential inhibitor for mild steel in 2 M HCl solutions by electrochemical impedance spectroscopy, weight loss, and polarization methods. Results obtained showed that the highest inhibition efficacy of 97.8% was obtained with a 500 ppm concentration of the waste. The potentiodynamic polarization test shows that the waste behaves as a mixed inhibitor. The electrochemical result shows that the charge-transfer resistance was increased, while, current density decreased with inhibitor in the 2 M HCl solutions. The inhibition performance of the waste increased with increasing concentration at the studied inhibitor dosages, the inhibitor molecules' adsorption on the metal fits the Langmuir adsorption isotherms. The experimental results showed that the waste products significantly improved resistance to wear. In addition, excellent toughness, high hardness, preferable adhesion, and good corrosion resistance also contributed to improve the tribological properties. The scanning electron microscope equipped with energy dispersive X-ray spectroscopy test confirms the protection of the mild steel in the HCl solutions. The results derived in this paper could prove highly beneficial and provide fundamental insights about the efficient use of agro-waste as an effective inhibitor, as well as stimulate the industrial application of agro-waste on a large scale.

8:20am **A1-3-TuM-2 Study of Materials and Coatings for Use in High Temperature $CO_2$ Environments***, **Jianliang Lin**,* Southwest Research Institute, USA

Oxy-fuel sCO2 power cycles are a transformational technology for the energy industry, providing higher efficiency heat source energy conversion for conventional and alternative energy sources. However, the technology requires advanced thermal management/protection systems to accommodate high temperatures for turbine critical components, e.g. nozzles and blades. The paper presents a study of NiCr based alloys and protective coatings for use in $CO_2$ environments using a high temperature thermal cyclic test rig. The thermal cyclic test was performed on uncoated and coated coupon samples in ambient atmosphere and $CO_2$ environment at 800 $^oC$ and 1150 $^oC$, respectively. One testing cycle includes 50 min annealing at peak temperature and 10 min cooling in air. The tested NiCr based alloys include Haynes 230, 625 alloy, HR-120 alloy, Inconel 718, and C22 alloy. The coatings include a nanocrystlline MCrAlY coating with a TiN diffusion barrier which was deposited using plasma enhanced magnetron sputtering (PEMS) technique, and a thermal barrier coating (TBC) system (MCrAlY bond coat and YSZ top coat) deposited by air plasma spray (APS).The nanocrystlline MCrAlY coating and TBC aimed at providing thermal and oxidation protection for different turbine critical components that see low temperature (e.g. 800 $^oC$) and high temperature (e.g. 1150 $^oC$), respectively. During the thermal cyclic tests, accumulative mass changes of the test coupons were recorded. The microstructure, chemistry, and phase changes of alloys and coatings after thermal cyclic tests were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS), and X-ray diffraction (XRD). The results showed that all uncoated alloys exhibited severe oxidation and degradation at 800 $^oC$. The nanocrystlline MCrAlY coating alone provided sufficient thermal/oxidation protection for all alloys from 800 $^oC$ to 1050 $^oC$ in ambient atmosphere and $CO_2$ environment. However, additional TBC is needed for protecting the alloys for higher temperatures (>1150 $^oC$).

8:40am **A1-3-TuM-3 Liquid Aluminum-Induced Wear of Ni-Based Superalloy at Elevated Temperatures***, **Hongfei Liu**,* Institute of Materials Research and Engineering (IMRE), A*STAR (Agency for Science, Technology and Research), Singapore*; N. Gong,* Institute of Materials Research and Engineering (IMRE), Singapore*; R. Karyappa, T. Meng,* Institute of Materials Science and Engineering (IMRE), Singapore

Ni-based superalloys have long been developed for structural components towards high-temperature applications, e.g., turbine blades, incineration plants, nuclear reaction plants, etc., due to their high mechanical strength and stable chemistry. On the other hand, along with the rapid development in additive manufacturing (AM) and remanufacturing of metal alloys in the past decades, electrochemical corrosion and hot corrosion have been extensively applied for testing and evaluating the chemical stabilities of AM-superalloys, in comparison with their competitors fabricated by traditional methods, at room and elevated temperatures.

Liquid metal has been employed in heat exchanger at high temperatures due to its higher thermal compacity than other media, e.g., water. In comparison to high-temperature oxidation and hot corrosion studies, liquid metal-induced wear of Ni-based superalloy is relatively less in the literature.

We have recently studied liquid aluminum-induced wear of Ni-based single crystal superalloys, addressed atomic diffusions and surficial cracks after cooling down from high temperatures. In this presentation, we will be discussing the experimental results and their related mechanisms.

9:00am **A1-3-TuM-4 Characteristics and Resistance of CVD Hafnium Carbide Coating in Extreme Environments***, **Hyeon-Geun Lee**, J. Lee, D. Kim, B. Jun, W. Kim, J. Park,* Korea Atomic Energy Research Institute, Republic of Korea

Hafnium carbide (HfC) has a high melting point and excellent resistance to ablation, corrosion, and mechanical/thermal stress. HfC coating is mainly considered to ultra-high temperature protective coating for aerospace application. HfC coating has strong anti-ablation ability due to high melting point, outstanding mechanical properties, superior oxidation resistance, absence of phase change at high temperature. Also, its favorable performance makes it possible to expect resistance in other extreme environments. Recently, in the field of nuclear power research, research on accident tolerant fuel (ATF) system and new generation power plant system including molten salt reactor (MSR) is in the spotlight. Structure materials are exposed to harsh environments such as hydrothermal corrosion and high temperature steam oxidation in ATF system and high temperature molten salt corrosion in MSR system. Various corrosion and oxidation resistance coatings including metal, ceramics, and hybrid coating that can protect structural materials in these extreme environments have been studied. In this study, characteristics and resistance of CVD hafnium carbide coating in various corrosion and oxidation environments were studied. Chemical vapor deposition (CVD) can provide the high purity dense coating with excellent crystallinity and uniformity. A highly crystalline dense HfC which contains a small amount excess carbon is uniformly deposited on graphite substrate using low pressure CVD from $HfCl_4$-$C_3H_6$-$H_2$ system. High temperature oxidation and ablation properties of CVD HfC coating were investigated. Hydrothermal corrosion evaluation is carried out using autoclave at 360 $^oC$, 19 MPa condition. The steam oxidation resistance was investigated at up to 1600 $^oC$ temperature with maximum 200 cm/s flow steam condition. Corrosion and oxidation resistance of HfC were analyzed compared to SiC, which is known to be excellent. High temperature molten chloride salt corrosion experiment was conducted at 650 $^oC$ in the controlled oxygen and moisture environments. The possibility of CVD HfC coating as a corrosion resistant coating of metal structural material were researched.

9:20am **A1-3-TuM-5 High Temperature Corrosion Protection of Zirconium Fuel Rods in Nuclear Reactors by Nanocrystalline Diamond (Ncd) Layers***, **Frantisek Fendrych**,* Institute of Physics Academy of Sciences of the Czech Republic

**Motivation**

Nanocrystaline diamond (NCD) film can be utilized as a protective coating for zirconium alloy (Zircaloy2) nuclear fuel cladding (NFC) of nuclear reactors. One big disadvantage of Zircaloy2 is that it reacts with water steam and during this (oxidative) reaction releases hydrogen gas, which partly diffuses into the alloy forming zirconium hydrides. Moreover, the large production of hydrogen gas can result into catastrophic hydrogen-air explosions (as occurred in the recent Fukushima accident, March 11, 2011).

**Plasma CVD reactor**

Diffuse plasma in the linear antennas microwave plasma enhanced CVD reactor was used for coating of cylindrical Zircaloy2 rods with NCD films. The combination of the linear antennas arrangement and the use of low pressures, > 1 mbar, a diffuse large area plasma is formed enabling large area 3D NCD deposition.

**Testing of the protective NCD films**

We have successfully demonstrated the possibility to cover a cylindrical rod-shaped Zircaloy2 nuclear fuel cladding by a 300 nm thick protective NCD layer using the linear antennas microwave plasma enhanced CVD. NCD coated Zircaloy2 rods underwent a set of corrosion tests, namely a reactor irradiation test and hot steam oxidation. SEM, Raman, XRD, XPS were employed. Oxidation of NCD coated and uncoated ZIRLO at 1000 °C is presented in supplemental document on **Figs.1,2**. It confirms that a thin NCD layer can serve as a anticorrosion protective coating on NFCs in the harsh environment of a nuclear reactor at substantially elevated temperatures.

**Conclusions**

Zirconium alloy ZIRLO of nuclear fuel cladding was covered by 300 nm thick protective nanocrystalline diamond NCD layer using special Linear Antennas pulsed MicroWave Plasma Enhanced CVD deposition technique. The NCD layer protects ZIRLO rods surface against hydrogen penetration and against oxidation during standard reactor run at about300 °C hot water steam and significantly decreases both in accidental case of overheating up to 800 – 1100 °C. NCD anticorrosion protection can up to 40% prolong lifetime of ZIRLO fuel rods and consequently enhances the uranium dioxide UO2 nuclear fuel burnup what leads to more efficient use of nuclear fuel in reactors. Final NCD/ZIRLO samples are longtime (for 2 years) tested by Westinghouse for real permanent run in Halden Norway experimental nuclear reactor. Application of presented research results for anticorrosion protection of power stations nuclear reactorsis proposed in EU and USA patents **[1,2]**.

**References**

**[1]** EU Patent No. 3047046 / 2020, WO 2015039636, A1, 2015, PCT/2014/000101.

**[2]** USA Patent No. 10916352 / 2021, WRB-IP, Ref. 000036-016; U.S. App. 15/022,536, 2021.

9:40am **A1-3-TuM-6 Effect of Vacuum Annealing on the Residual Stress of ZrN Thin Film deposited on Ni-based Superalloy Haynes 282***, **Kuan-Che Lan**, C. Li,* National Tsing Hua University, Taiwan*; H. Tung,* Institute of Nuclear Energy Research, Taiwan

Transition metal nitride thin films deposited using physical vapor deposition (PVD) methods tend to experience a significant amount of residual stress. The existence of residual stresses in thin films can do influence on their mechanical properties greatly. It is believed that the processing of heat treatment can help relief the residual stress in a crystalline material. To study the effect of heat treatment after a PVD method, ZrN thin films deposited using the DC magnetron sputtering system on both Si and nickel-based superalloy Haynes 282 substrates was annealed in vacuum ($4\times10^{-6}$ Torr) at 950˚C. After vacuum annealing, the film thickness, the crystallographic structure and depth compositional distribution of the annealed ZrN thin film will be characterized by scanning electron microscope, the X-ray diffraction and Auger electron spectroscopy, respectively. Averaged X-ray strain method will be also applied to analyze the residual stress of the ZrN thin film on Haynes 282.

10:00am **A1-3-TuM-7 Study at Pilot Plant Scale on Biomass Corrosion Resistance of FeCr and CoCrMo Coatings Applied by HVOF***, M. de Miguel Gamo, G. García Martín, M. Lasanta Carrasco, M. Lambrecht,* Universidad Complutense de Madrid, Spain*; F. Gonçalves,* Teandm - tecnologia engenharia e materiais s.a, Portugal*; M. Sousa,* teandm - tecnologia engenharia e materiais s.a, Portugal*; A. Bahillo, M. Benito,* Centro de Investigaciones Energéticas, Medioambientales y Tecnológicas (CIEMAT), Spain*; **Francisco Javier Pérez Trujillo**,* Universidad Complutense de Madrid, Spain

The replacement of coal by biomass combustion is considered as a promising option to reduce the emissions associated to this fossil energy source. At the same time, the energetic use of the biomass contributes to solve the problem of waste disposal. On the other hand, this renewable technology presents two main disadvantages: (1) the cost of biomass is higher than coal, what leads to a higher cost of the electricity production, (2) biomass combustion environment is extremely corrosive induced by the high amount of chlorine present in the fuel (gas) and/or the present of alkali and heavy metals in condensed deposits. The aggressive conditions commonly imply the use of austenitic or nickel-based alloys that increases the investment required. An alternative to mitigate corrosion and allow operation at more aggressive conditions, is the use of highly-corrosion resistant coatings over lower cost alloys, such as ferritic steels.

The present study compares the biomass corrosion behavior of two different coatings, FeCr and CoCrMo, applied by High Velocity Oxy-fuel (HVOF) on a 12%Cr steel to improve its oxidation resistance. The coated specimens were tested in a pilot plant installation and exposed to the flue gases from the combustion of two different agricultural biomasses (eucalyptus and wheat straw) for 2000 h at 600°C. The samples were weight monitoring at different times during the testsand characterized before and after oxidation tests by X-ray diffraction (XRD) and scanning electron microscopy with energy dispersive spectroscopy (SEM/EDS). At the end of the exposures, both coatings, FeCr and CoCrMo, have shown a significant corrosion layer. Although, when the results were compared with the 12%Cr steel uncoated, it was confirmed that the application of both coatings reduces the weight gain of the steel, increasing its corrosion resistance. The obtained results make these coatings a promising alternative, that should be further investigated from the mechanical perspective, for enhancing the lifetime of in-service power plant components.

10:20am **A1-3-TuM-8 Sol-Gel Coating to Protect Materials Exposed Under Carbonates Used as a Thermal Energy Storage System in Central Tower Power Plants***, **Gustavo García Martín**, M. de Miguel Gamo, M. Lasanta Carrasco, M. Lambrecht, F. Pérez Trujillo,* Universidad Complutense de Madrid, Spain

Zirconia-based sol-gel protective coatings have emerged as one of the most viable solutions to protect steels against molten salt corrosion in Concentrated Solar Power plants with nitrates as thermal energy storage. Thermal energy is used in the production of steam and electricity production subsequently, by means of the movement of a conventional turbine (Rankine cycle)

Central Tower design is a suitable technology to use new molten salts with higher thermal stability than nitrates, such as carbonates, which would allow plants to generate a higher amount of water vapour per unit of time, thus a higher conversion to electricity. Central receivers made of nickel-based material will increase the temperature from 565ºC with nitrates up to 800ºC with carbonates. Particularly, the outstanding eutectic ternary $Li_2CO_3$-$Na_2CO_3$-$K_2CO_3$ is presented as a real alternative nowadays. The drawback is its corrosion potential, hence protective coatings are being studied to enhance the endurance toward a levelized cost electricity (LCoE) reduction.

In support of these objectives, this work aimed at developing zirconia-based sol-gel protective coatings on the nickel-based alloy INCONEL 617 (Ni 53.28 wt.%, Cr 21.5 wt.%, Mo 8.80 wt.%) and the low chromo content alloy P91 (Cr 9.3· wt.%). Inconel would be used in high-temperature equipment such as receivers, exchangers, and high-thermal storage tanks. On the other hand, the ferritic-martensitic alloy might be used inlower-temperature parts, for instance, cold-temperature storage tanks, which could operate at 480ºC. Corrosion tests were performed at 480°C and 700°C up to 1000 h results were supported by gravimetric and microstructural characterizations. All results were compared to the uncoated steels. The results showed the promising behaviour of the coated substrates.

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