30 Advances in Corrosion and Surface Modifications

Nanoscale Corrosion Characterization of Surface Hardened Martensitic Stainless Steel: Resolving Local Contributions to Bulk Materials Performance, MICHAEL HURLEY*, COREY EFAW, PAUL DAVIS, ARMEN KVRYAN, BRIELLE IBE, and NICK CARTER (Micron School of Materials Science and Engineering, Boise State University, Boise, ID; mihurley@boisestate.edu, coreyefaw@u.boisestate.edu, pauldavis2@boisestate.edu, armenkvryan@u.boisestate.edu, brielleibe@u.boisestate.edu, nickcarter@u.boisestate.edu)

Martensitic stainless steels are attractive for bearing applications due to their high corrosion resistance and ability to be surface hardened via carburizing heat treatments. Here three different carburizing heat treatments were applied to UNS S42670: a high-temperature temper (HTT), a low-temperature temper (LTT), and carbo-nitriding (CN). Recent advances in characterization tools have progressed the means to resolve features that control corrosion mechanisms. However, many localized techniques do not provide sub-micron spatial resolution or non-destructive analysis. Scanning Kelvin probe force microscopy (SKPFM) has presented a non-destructive alternative to better understand corrosion mechanisms on the micro to nano-scale. SKPFM maps the Volta potential difference (VPD) between Kelvin probe and surface. VPD has been directly correlated to corrosion potentials, and thus provides strong predictability of corrosion mechanisms. When co-localized with SEM/EDS, Volta potentials can be correlated to elemental composition and thus galvanic-driven initiation phases. For martensitic stainless steels, the VPD between the matrix and carbides, revealed a 90–200 mV difference between the two phases. Corrosion progression was monitored on the nanoscale via SKPFM and in situ atomic force microscopy (AFM), revealing different corrosion modes among heat treatments that predicted bulk corrosion behavior in electrochemical testing. HTT outperforms LTT and CN in wear testing and thus is recommended for non-corrosive aerospace applications, whereas CN is recommended for corrosion-prone applications as it exhibits exceptional corrosion resistance. The results reported here support the use of scanning probe microscopy for predicting bulk corrosion behavior by measuring nanoscale surface differences in properties between carbides and the surrounding matrix.

Electrochemical Characterization of Titanium Alloys Subjected to an Atmospheric Pressure Plasma Treatment, KEVIN ROBLES1*, SARA MARGALA2, NINA ABRAMZON2, and VILUPANUR RAVI1 (1Department of Chemical and Materials Engineering, 2Department of Physics and Astronomy, California State Polytechnic University, Pomona, Pomona, CA; krobles@cpp.edu, sgmargala@cpp.edu, nabramzon@cpp.edu, vravi@cpp.edu).

Titanium and its alloys are used in various industries ranging from aerospace components to biomedical implants. Ti-6Al-4V (UNS R56400; Ti64) has been used as a structural biomaterial due to its excellent corrosion resistance, biocompatibility, high strength and low Young’s modulus. A known issue with Ti64 is the release of harmful metal cations that negatively impact surrounding tissue and cause adverse health effects. Previous research found that Ti64 with boron additions, 0.01 to 1.09 weight percent, improved the corrosion resistance; however, surface modification techniques, such as atmospheric radio frequency nitriding (CN), have also been considered in order to further improve the corrosion resistance of these titanium alloys. In this study, Ti64 with low levels of boron additions were plasma treated and characterized using electrochemical methods. Test coupons of three different titanium alloys, i.e., Ti6Al4V, Ti6Al4V.01B and Ti6Al4V 1.09B (all in mass%), were polished to a mirror-like finish using standard metallographic procedures. These alloy coupons were exposed to an atmospheric pressure plasma containing a mixture of helium and oxygen for 5 seconds. Electrochemical characterization of the pre and post plasma treated alloys were carried out in deaerated 3.5 wt% sodium chloride solution. The electrochemical tests included three distinct stages: (i) a 1 h open circuit exposure during which voltage vs time data (OCV) were obtained (ii) a linear polarization scan from -30 mV to +30 mV relative to the OCV to obtain the linear polarization resistance (LPR) and (iii) a Tafel plot from -400mV to + 400 mV relative to the OCV. Localized corrosion testing, utilizing a scanning droplet cell, was performed to characterize the change in the corrosion behavior of the plasma treated materials over time.

High Temperature Corrosion, VILUPANUR A. RAVI (Department of Chemical and Materials Engineering, Cal Poly Pomona, Pomona, CA; vravi@cpp.edu).

Corrosion is a complex phenomenon involving (predominantly) metallic alloys and the surrounding environment. The various forms of corrosion suffered by metallic materials in aqueous environments have been studied extensively and codified. In contrast, corrosion at high temperatures involves gaseous environments and/or electrolytes like molten salts. Studies in this area are more limited in comparison to the literature in aqueous environments. There is, however, a need for continued studies in this area due to the needs of a broad range of industries including the chemical process, petrochemical refining, waste incineration and power generation industries. Some examples of high temperature corrosion phenomena are: high temperature oxidation in air, carbon dioxide, steam, etc., sulfidation in atmospheres containing sulfur dioxide, hydrogen sulfide, sulfur
vapor, etc., carburization, metal dusting, halogen attack, hot corrosion, i.e., accelerated corrosion under thin molten salt films and molten salt corrosion or corrosion in bulk molten salt – full immersion, etc. In this talk, I will discuss some of these forms of corrosion and potential methods to defend against them.

**Aluminizing Co-base Superalloys**, **KAILEY HANAN†**, **ANNETTE WAGNER**1, **PRAFULL PANDEY**2, **KAMANIO CHATTOPADHYAY**3, and **VILUPANUR RAVI**1 (†Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, Pomona, CA; 2Department of Materials Engineering, Indian Institute of Science, Bangalore, Bengaluru, Karnataka 560012, India; kahanan@cpp.edu, alwagner@cpp.edu, prafull1011@gmail.com, kamanio@iisc.ac.in, vravi@cpp.edu).

Cobalt-base superalloys are used in applications requiring strength and corrosion resistance at high temperatures, e.g., in turbine hot section stationary components, such as the vanes. While the materials selection for this application is based on the physical and mechanical properties of the alloys, their resistance to the local environment is a different issue and more specifically, it is a surface issue. Modifying the surface of these alloys without altering their bulk properties is an effective approach to defending them against the hostile environments in which they need to function. In this study, novel cobalt-based superalloys were surface-modified using the halide-activated pack cementation (HAPC) method. This technique is a modified chemical vapor deposition process that deposits the desired element on the surface of the metallic alloy through a series of processes including chemical reactions and mass transport of halide vapor species that occur in the pack surrounding the material to be surface-modified. Once deposited, the coating element subsequently diffuses into the substrate transforming the surface into a different material with distinct microstructural changes. Under oxidizing conditions, the surface-modified alloy forms an oxide layer that acts as a barrier to diffusion and protects the underlying alloy. The objective of this work was to compare the differences in the morphology of the coating produced on two Co-Ni-Al-Mo-Ti alloys. Both alloys had similar compositions, with one series containing ~2 at% tantalum, and the other containing ~2 at% niobium. The substrates were ground to a 600 grit finish prior to the HAPC treatment at 850°C for 9 hours. Coating morphologies were compared using optical microscopy, polarized light microscopy, X-ray diffraction, and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS). Results thus far indicate that the additions of Ta and Nb influence the coating morphology in different ways. Multi-layer coatings were developed on both alloys, with thicker outer layers, a homogenous middle layer, and a very thin inner diffusion zone. However, the morphology of the layers differ in the two cases and will be discussed. Preliminary results of cyclic oxidation studies will be reported.

**Early Stage Oxidation of UNS N06230 and UNS N07214 in Dry and Humid Conditions**, **NICHOLAS URY†**, **ANETTE WAGNER**1, **VINAY DEODESHMUKH**2 and **VILUPANUR RAVI**1 (†Department of Chemical and Materials Engineering, California State Polytechnic University, Pomona, Pomona, CA; 2Haynes International, Kokomo, IN; neury@cpp.edu, alwagner@cpp.edu, vdeoodeshmukh@haynesintl.com, vravi@cpp.edu).

Nickel base alloys are widely used in industry for high temperature applications. Chromium and aluminum are added to these alloys to form protective layers of chromium oxide (chromia) or aluminum oxide ( alumina). In dry air, the behavior of chromia- and alumina-forming alloys can be predictable. However, in atmospheres containing a significant amount of water vapor, these predications are not applicable. Therefore, a comparative study was conducted on the oxidation behavior of a chromia- and an alumina- former in dry and wet air to better understand the effects of water vapor in the oxidative atmosphere. UNS N06230, a chromia-former, and UNS N07214, an alumina former, were oxidized at 1000°C in dry and wet air (15 volume% H₂O) for 1 minute, 10 minutes; and 1, 5, 10 and 100 hours, in a thermogravimetric analyzer. The oxidized coupons were characterized using X-ray diffraction and scanning electron microscopy. In these early stage oxidation experiments, the UNS N07214 (alumina former) had a lower oxidation rate relative to the UNS N06230 (chromia former). The alumina former showed a more complex behavior in these early stages of oxidation relative to the chromia former. The results will be presented and their significance discussed.