PROTECTION SYSTEMS: CORROSION RESISTANT COATINGS

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ABSTRACT

Material loss caused by exposure to the severe operating environments in gasifiers (slagging and non-slagging), industrial waste incinerators, and other advanced fossil or biomass-fueled power systems results in reduced service life and reliability, as well as increased operating costs. This project aims to improve performance of materials by combining intelligent design with colloid science and coating technology to develop cost-effective materials and processes for optimum performance and maximum service life in their specific fossil environment. Lower cost methods and novel approaches of applying coatings to metals are being explored to meet more near-term goals. Thus, the development of novel coatings utilizing low-cost aqueous processing methods such as dip coating is being pursued. Colloidal processing of metallic particles in aqueous suspension offers an economic route for forming uniform, metallic coatings on complex-shaped components via a simple process. The issues of adhesion, uniformity and processing parameters on resulting material phases, the effective corrosion resistance in specified fossil environments, and the mechanical properties at use temperatures will be the technical challenges that must be addressed in order to prove feasibility for metallic-based systems. A review of the ORNL dip coating process for application of coatings onto ferritic martensitic alloys will be discussed.

INTRODUCTION

Advanced fossil energy processes have hostile environments with temperatures as high as 1550°C and atmospheres that contain water vapor, sulfur, nitrogen, trace heavy metals, molten slag and alkali salts. Ceramic and metallic material systems can potentially play important roles in the harsh fossil environments. The metal systems of interest are ferritic martensitic steels to address corrosion issues in superheaters, boilers, heat exchangers, turbines, and Ni-based super alloys to address corrosion issues in ultrasupercritical systems.

Coatings for both ceramic and metallic systems have been long utilized for protection purposes in many industries. Some applications include paint (architectural, automotive, marine), environmental barriers for micro turbines and other distributed energy systems, and thermal barriers for fossil and distributed energy systems. There are many techniques available to fabricate layers (coatings) of varying thicknesses. Some of these include plasma vapor deposition (PVD), electron beam – plasma vapor deposition (EB-PVD), chemical vapor deposition (CVD), pack cementation, and slurry or dip coating (1-7). With the exception of pack cementation and slurry coating, these processes are typically costly, line of sight techniques which do not lend themselves to coating large, three dimensional parts (i.e. nonconformal surfaces). Pack cementation is very effective for non-complex stoichiometric coating material systems while slurry coating can handle a wider variety of material systems.

In metallic systems, one advantage of a coating is that the substrate alloy can be optimized for properties other than corrosion resistance (i.e. ductility, formability, creep strength, etc) (8-9). The technical challenge is that the physical, chemical, and mechanical differences between the substrate and the coating can lead to detrimental interactions, which can limit lifetime. Interdiffusion between coating and substrate can result in the formation of brittle intermetallic phases or the loss of protective scale-forming elements. For example, in thermal barrier coatings

(TBC)/superalloy systems, a major problem is the loss of Al from the bond coat to the substrate superalloy over time at temperature, which ultimately contributes to an inability to maintain Al_2O_3 growth and subsequent coating failure (6, 10). Thus, the design of the protective coatings in consideration of the substrate has received increased attention in recent years. For example, recent work by Gleeson et al has identified Ni-Al-Pt bond coat compositions for which Al diffuses from the substrate superalloy into the coating, helping to maintain a reservoir of Al for Al_2O_3 formation by the coating, rather than loss of Al from the coating alloy to the substrate. Typically, these Al coatings are applied after annealing of the metal and require further post heat treatment processing to convert the Al to Al_2O_3. This step can degrade physical properties of the metal while adding additional processing time and expense to the process. A slurry coating process may allow changes to current processing steps by either limiting the processing temperatures that the coating/metal interface sees (slurry coating is a room temperature process) and/or by reducing steps (i.e., combining the coating and metal annealing process into one). If a less expensive, non-line of sight process can be utilized to deposit a metallic coating or a film that will react to form the appropriate metal or ceramic phase directly, control of the metal's physical properties can be maintained or optimized while minimizing processing time and/or expense. This has been demonstrated recently by Agüero who has used aluminide slurries to coat ferritic martensitic steels (7).

Colloidal processing offers a low cost alternative approach for producing uniform coatings on complex-shaped components via a simple dip coating process (i.e., the ORNL slurry coating process) (4-5). Control of the rheological behavior of the suspension by tailoring interparticle (or surface) forces is paramount to achieve a high quality defect free coating. In aqueous-based suspensions long-range attractive van der Waals forces must be balanced by repulsive forces to tailor the desired degree of suspension stability. Typically, ionizable polymeric dispersants, or polyelectrolytes, are used to modify the surface of particles to impart repulsive electrosteric forces (11-12).

This year the work on the development of concentrated aqueous suspensions comprised of aluminum particles was evaluated. This effort focused on applying Al coatings to ferritic, martensitic alloys (Fe-9Cr-1Mo, T91) using a dip or slurry coating process. The coatings were heat treated at varying temperatures to determine the robustness of the processing conditions (which will enable alternative coating windows in the alloying process).

EXPERIMENTAL PROCEDURE

Aluminum, (H10, Valimet Inc., Stockton, CA) was used as the metal powder in this study. The aluminum powder had an average particle size of ~ 13.19 μm and surface area of 0.4475 m^2/g, determined using dynamic light scattering (Horiba, Inc., Kyoto, Japan) and B.E.T. (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL), respectively. Polyacrylic acid (PAA, 450kg/mol, Aldrich Chemicals, Milwaukee, WI), an anionic polyelectrolyte, was used as the dispersant and PL001 (Polymer Innovations, Inc., Vista, CA) as the rheological modifier for the Al system. Water purity was measured using inductively coupled plasma mass spectroscopy (ICPMS, X Series 2, Thermo Fisher Scientific, Inc., Waltham, MA). The standards (QCS26, High Purity Standards, Charleston, SC) and the nitric acid matrix (Ultrex Pure., J.T. Baker, Phillipsburg, NJ) were used to calibrate the ICPMS. Contact angle was measured using the Sessile drop technique. A droplet of Al slurry was dropped onto the surface of commercial ferritic (Fe-9Cr-1Mo, T91) substrates, and the wetting angle was calculated using Rhino (McNeel North America, Seattle, WA).

Zeta potential measurements were carried out on the Al particles in dilute aqueous suspension using capillary electrophoresis (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK). Dilute suspensions (10^{-3} vol% solids) were prepared by adding the appropriate amount of powder to aqueous, KNO_3 solutions (0.001 *M*) of varying pH ranging from 2 to 11. The solutions were adjusted to the appropriate pH using nitric acid or ammonium hydroxide.

Rheological measurements were carried out on concentrated aluminum suspensions using a controlled-stress rheometer (Rheometric Scientific SR5, TA Instruments, New Castle, DE) fitted with a concentric cylinder. Concentrated aluminum suspensions (5 vol% solids) were formulated by mixing an appropriate amount of aluminum powder into aqueous solutions (pH 7) of varying PAA concentration. A solvent trap was used to minimize the evaporation of water. In this way, variations in sample handling were minimized to ensure

reproducibility of the data. Stress viscometry measurements were carried out by logarithmically ramping an applied shear stress from 0.025 to 200 Pa. A delay time of 60 s between consecutive data acquisition events was used in this study.

Commercial T91 (Fe-9.3at.%Cr-0.56Mo-0.46Mn-0.26V-0.55Si-0.15Ni-0.46C-0.22N-0.005S) was machined into test specimens. T91 substrates that were 11.9 mm x 19.1 mm x 1.7 mm in size were dipped into the aluminum suspensions of varying Al concentration at a fixed PAA concentration (1.15 mg/m^2). All of the coated substrates were dried under ambient conditions and sintered at varying temperatures in an argon atmosphere. Sintered samples were examined by scanning electron microscopy (SEM) and by electron probe microanalysis (EPMA) using wavelength dispersive x-ray analysis.

RESULTS AND DISCUSSION

ZETA POTENTIAL

Zeta potential measurements were carried out on dilute aluminum and alumina suspensions (10^{-3} vol% solids in deionized water) of varying pH and the results are shown in Fig. 1. The isoelectric point (IEP) of aluminum was initially observed at pH 3. However, the aluminum particle surface underwent charge reversal after pH 5, and a sharp increase in zeta potential to 10.9 mV occurred. This phenomenon may indicate the formation of a passive hydroxide layer on the surface of the aluminum particles. This theory is reinforced by comparing the zeta potential curve of an aluminum oxide (Al_2O_3) powder (AKP 30, Sumitomo, Japan). The zeta potential of the Al_2O_3 closely matches the behavior seen in the Al powder at higher pH's. The net positive surface potential at pH 9 of the Al powder indicates that an anionic polyelectrolyte (e.g., the PAA dispersant) that is fully (negatively) charged at these pH conditions will strongly adsorb to the surface of the particles. The adsorbed PAA, in turn, should promote dispersion of the particles. Based on our findings, all of the rheological studies were completed with PAA as the dispersant.

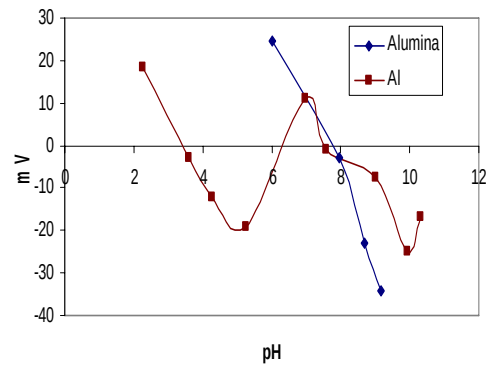

Fig. 1. Zeta potential as a function of pH for dilute aluminum and alumina suspensions (10^{-3} vol% solids).

RHEOLOGICAL BEHAVIOR

Previously work demonstrated that ceramic gels with slightly shear-thinning flow behavior were identified as the optimum rheological conditions for coating dense, ceramic substrates with the ceramic suspensions (4-5). The same behavior was maintained in the Al slurries in this study to achieve the desired uniform coating surfaces remained constant. Previous work also demonstrated that the effect of small amounts of contamination from the organic processing aids and the water purity affected the slurry flow behavior and ultimately the gel structure and resulting coating microstructure. In the silicate-based oxide material systems evaluated previously, a gel structure would form in the resulting coating in the presence of minor amounts of contaminates, such as barium, strontium lanthanum, copper, zinc and lead. Thus, water purity was tested in order to eliminate this as a variable. Finally, the effect of contamination from two separate water sources was evaluated in this study.

Water for all slurries was obtained from two sources; a deionized water purifier (E-Pure, Barnstead) and a steam operated distiller system (Barnstead). It was assumed that the distilled water would contain less contamination than the deionized water (DI). As seen in Table 1, the level of contamination in the distilled water (Dist) source was actually higher. The amount of contamination although low (in the parts per billion) may be enough to cause gelation, wetting or viscosity in slurries with materials sensitive to hydrolysis and gelation, such as doped silicates or alumina. Since the aluminum powder being used in this study appears to have an alumina or aluminum hydroxide surface as seen from the zeta potential curves discussed previously, the water source of the slurry will remain an issue until further analysis can be completed.

Table 1. ICPMS Analysis of Deionized and Distilled Water Sources.

Isotope	Deionized Water (ppb)	Distilled Water (ppb)
Na	2	4
Al	< 2	48
K	2.8	4
Mn	< 2	53.2
Fe	< 2	.91
Ni	< 2	130
Cu	< 2	85.7
Zn	9	550
Sr	20	.09
Ba	1.2	1.2
Pb	.44	545

Rheological measurements were carried out on the Al suspensions of varying solids concentration in both deionized (DI) and distilled (Dist) water as shown by the plot of apparent viscosity as a function of applied shear stress in Fig. 2. The PAA concentration was fixed at 1.15 mg PAA/m^2 Al. As anticipated, apparent viscosity increased with increasing Al concentration and the effect of the purity of the water source was not evident. Newtonian behavior was observed at 1 vol% solids, but slight shear thinning behavior was observed at solids loadings of 3 and 5 vol%, respectively. Due to the low solids concentration at the 1 vol % condition, Newtonian flow is not unexpected.

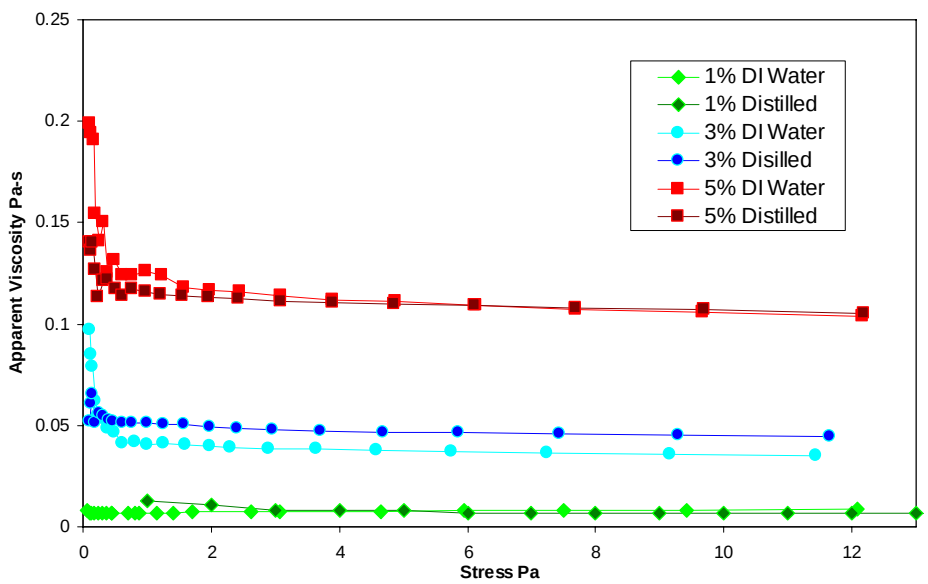

Fig. 2. Apparent viscosity as a function of shear stress for aluminum suspension of varying Al concentration.

COATING FORMATION

The effect of contamination from the deionized and the distilled water sources was not evident in the flow behavior. Consequently, the contact angle was measured using the Sessile drop technique to evaluate the effective wetting of the Al slurries as a function of solids loading and water source on the surface of the ferritic substrates. The effect of the water purity was much more evident in the Sessile drop studies. The distilled water based slurries had higher

contact angles or reduced wetting than the equivalent solids loading slurry made with deionized water as shown in Table 2. If gelation is occurring as a function of the added contamination, reduced wetting behavior would be anticipated. The contact angle also increased with increasing Al solids loading relative to the water source. This is also anticipated due to the relative increase in viscosity from the increased solids. An image of a representative Al slurry droplet on a T91 substrate is shown in Figure 3.

Figure 3. Representative Al slurry droplet on a T91 substrate.

Slurry (%Al)	Contact Angle
1% Š DI H_2O	25.21
1% Š Dist H_2O	41.52
5% Š DI H_2O	33.91
5% Š Dist H_2O	57.39

Table 2. Contact angle as a function of water source and Al solids loading.

For effective coating behavior, the balance of shear thinning behavior to maintain uniform coating thickness as well as low contact angles to improve wetting is critical. To physically determine the balance between rheology and wetting, substrates must be slurry coated, the substrate and the coating sintered, and the resulting coating microstructure (thickness, uniformity, and Al diffusion) characterized as a function of the densification properties (temperature and time). A baseline slurry was selected for all dipping and densification studies based on water purity, wetting and the rheology data. The Al slurry with the highest solids loading demonstrating shear thinning behavior and having the lowest contact angle was selected. Thus, T91 substrates were dipped into Al suspensions made with deionized water (5 vol% solids), and the resulting coating are displayed in Fig. 4. Adequate coating coverage was attained.

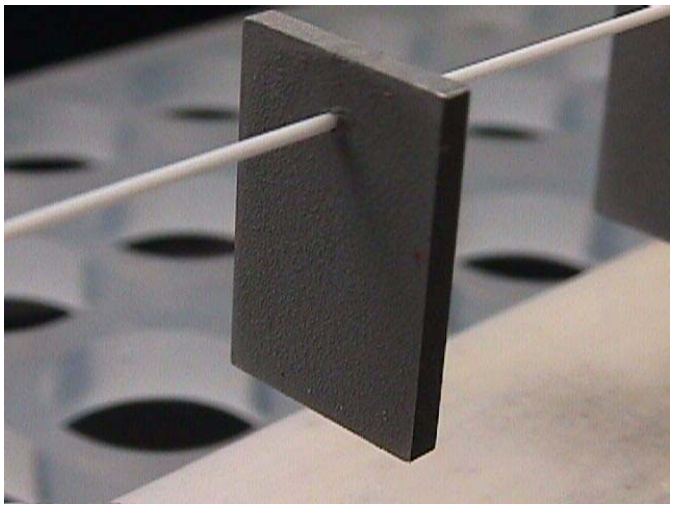

Figure 4. As-dipped Al coated T91 substrate.

SINTERING BEHAVIOR

All densification studies were carried out on T91 substrates dipped into Al suspension made with deionized water at 5 vol% Al solids loading. Sintering temperatures were selected based on typical ferritic steel processing conditions of 750°C and 1050°C. Coated substrates were sintered at these temperatures in Ar for two hours. After sintering at

750°C for 2 hours, a non-uniform layer of Al "islands" or nodules were visible across the surface of the substrates. The thickness of each of Al islands varied, however the average thickness was ~ 30 μm, as shown in Figure 5. Increasing the sintering temperature to 1050 °C yielded a uniform layer of Al-rich T91, with columnar grains (Figure 6) across the substrate with a maximum interdiffusion distance of Al up to 120 μm. It is not certain at this time why the formation of Al islands occurred, how the non-uniform islands diffuse so uniformly across the substrate at an increased temperature, or why the columnar grains form. These early results at 1050°C are encouraging however since the concentration of Al at the surface is ~9 atomic % (Figures 7 and 8). Figure 7 is a scanning electron micrograph of the area mapped using EPMA. Figure 8 shows the Al content as a function of depth into the T91 substrate for the Al coatings sintered at 1050°C. Pint et al. has reported that a minimum concentration of Al (~3.5 at%) is necessary to improve coating lifetimes (13). Further iterations are necessary to increase the concentration of the Al in the substrate and develop an understanding of how processing variables control Al diffusion concentration and depth.

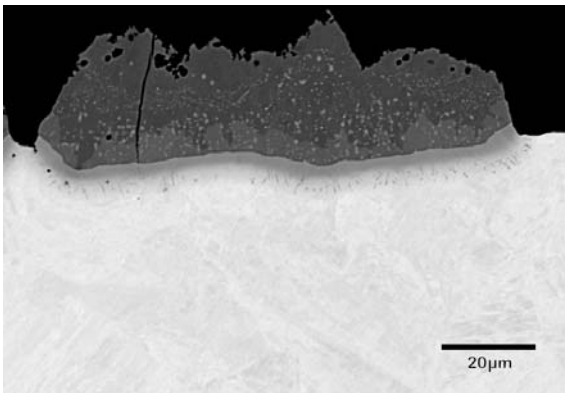

Figure 5. Scanning electron micrograph of Al coating on T91substrate after heat treatment to 750°C for 2 hours in an argon environment.

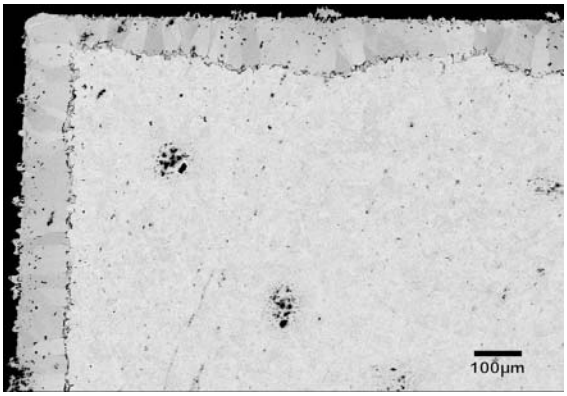

Figure 6. Scanning electron micrograph of Al coating on T91substrate after heat treatment to 1050°C for 2 hours in an argon environment.

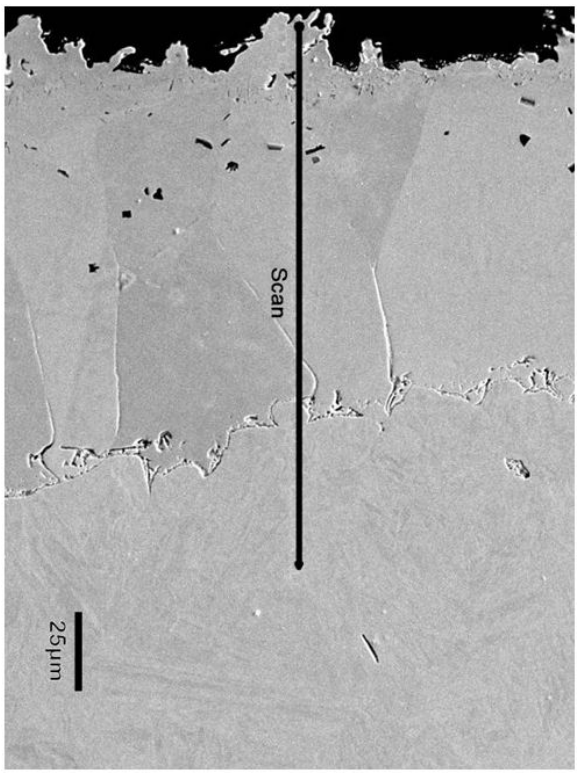

Figure 7. Scanning electron micrograph of EPMA scanned area for coating sintered at 1050°C for 2 hours in Ar.

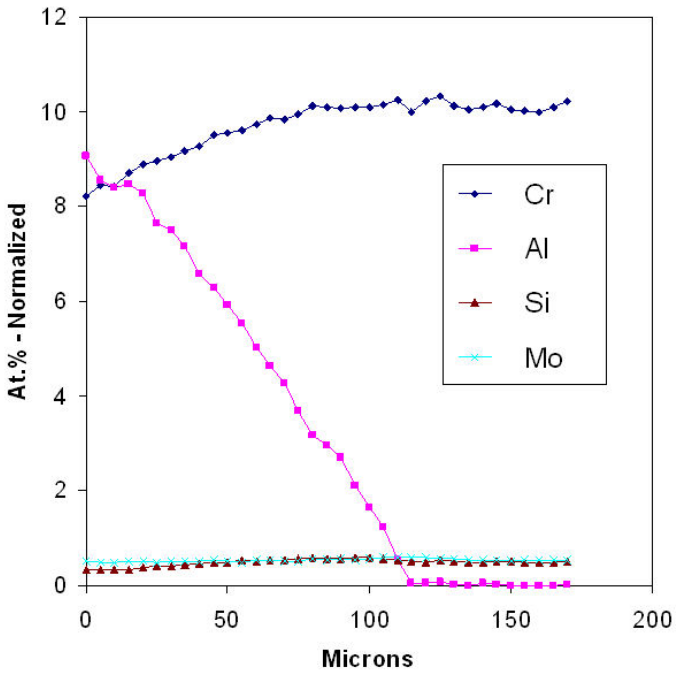

Figure 8. Al content by EPMA as a function of depth for coating sintered at 1050°C for 2 hours in Ar.

CONCLUSIONS

The ORNL slurry coating approach is a low-cost method to deposit protective layers on ferritic, martensitic steels for use in fossil energy applications. The surface of aluminum particles in aqueous suspension was characterized using zeta potential measurements. A polyelectrolyte dispersant was identified to modify the rheological behavior of aluminum suspensions. Wetting behavior of the aluminum slurries was altered by Al solids loadings and contamination from the water source. Sintering conditions were varied to examine their influence on coating quality and Al interdiffusion. Efforts are underway to optimize the properties of the slurry system and characterize the resulting corrosion properties.

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