CORROSION RESISTANT CERAMIC COATINGS

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ABSTRACT

Enhancing the output and economics of fossil energy conversion and combustion systems (gasifiers) by operating at higher temperatures, higher throughputs, and variable feed stocks, decreases the useful operating life of the materials used in these environments. The limiting factor for most "high temperature materials", i.e., ceramics, is the susceptibility to corrosion by molten slags, alkali metals, and gases in these harsh operating environments. In order to utilize the attractive properties of ceramic materials, such as their high temperature strength, additional measures must be employed to protect the materials to extend their service lifetimes. To address this issue, the development of novel coatings utilizing low-cost aqueous processing methods is being pursued. Colloidal processing of ceramic particles in aqueous suspension offers an economic route for forming uniform, thick ceramic coatings on complex-shaped components via a simple dip-coating process. Application of the ORNL dip coating process was examined for mullite coatings on sintered alpha silicon carbide substrates and the ARC developed chromia system on chromia refractory bricks. Early results of this work will be presented.

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. There are two classes of ceramics that can potentially play an important role in the harsh fossil environments: silicon-based, nonoxide ceramics (e.g. SiC and SiC/SiC composites) and non silicon-based oxide ceramics for refractory applications.

Silicon-based ceramics such as SiC or SiC/SiC composites are attractive for use in fossil environments for applications such as hot-gas filters, heat exchangers, and other devices for advanced energy producing

systems. They are candidates due to their higher temperature capability relative to metals, high thermal conductivity, retention of mechanical properties at operating temperatures, and excellent thermal shock resistance. A slow growing silica scale is the typical protection mechanism for the SiC material. This scale limits oxygen diffusion and thus prevents further attack of the substrate. A major drawback of SiC ceramics, however, is the susceptibility of the silica scale to volatilization and corrosion by water vapor and alkali salts such as Na_2SO_4 at high temperatures. This factor limits the applicability of SiC ceramics for extended service in many fossil energy conversion and combustion system environments.[1-3] Thus, the use of protective coatings (e.g. mullite) or the development of material with improved stability in these harsh environments is necessary.

Chromia-based (non silicon-based) refractory materials play an important role in thermal management for slagging and non-slagging gasifiers and are currently, the only feasible option for reaction containment in slagging gasifiers,[4-9] which are predicted to be at the heart of many of the Advanced Fossil Fuel Power Systems planned for the future. Although coal gasification has proven to be an efficient and relatively clean way to produce electricity, liquid fuels, and chemicals, it has not yet reached the level of reliability, availability, and maintainability that will lead to widespread market acceptance. Rapid refractory material loss caused by exposure to the severe operating environments present in gasifiers (i.e., elevated temperatures, pressures, corrosive slag and gas concentration) results in reduced refractory service life and directly impacts the on-line availability of the gasifier island to produce synthesis gas. Because the entire system must be shutdown to reline these materials, refractory service life has a direct impact on gasifier on-line availability. Attempts to enhance gasifier output and economics by operating at higher temperatures, with higher throughputs, and/or with variable feedstocks, put additional stress on the materials exposed to the operating environment, and typically result in a corresponding decrease in their useful service life. As a result, the reliability and economics of gasification as a means to generate electricity and other products are adversely impacted. For example, current generation high chromium-oxide refractories typically last between three and 18 months inside a gasifier, depending on the operating conditions and locations of the specific system.

To address the need for improved performance in gasifier lining materials, the Albany Research Center (ARC) has developed a modified chromia refractory brick that is designed specifically for longer life in the slagging gasifier environment.[9] Further improvements in refractory performance may also be gained through the addition of a coating, particularly if it is both slag resistant and economical to apply. The Oak Ridge National Laboratory (ORNL) slurry coating technology (described below) offers the opportunity to apply a dense, slag resistant ceramic layer to the modified refractory without significantly increasing production costs.

Colloidal processing of ceramic slurries offers a low cost alternative approach for producing uniform, thick ceramic coatings on complex-shaped components via a simple dip coating process (i.e., the ORNL slurry coating process). This approach has been demonstrated in many multi-disciplinary areas such as coatings (paints, glazes), fabrication of monolithic components (casting, deposition), and emulsions (gels, food additives, cosmetics). Control of the suspension rheological behavior is paramount to produce quality coatings and can be accomplished by tailoring interparticle (or surface) forces. In aqueous-based suspensions, long-range attractive van der Waals forces are ubiquitous and must be balanced by repulsive forces to tailor the desired degree of suspension stability. For example, ionizable polymeric dispersants, or polyelectrolytes, are commonly used to modify the surface of particles to impart repulsive electrosteric forces.[10, 11]

This year, concentrated, aqueous suspensions comprised of mullite and chromia particles were developed for use in a dip-coating process. Mullite and chromia were chosen to demonstrate the feasibility of these processes as their behavior is well-characterized in their respective fossil environments. The approach consists of zeta potential measurements as a function of pH to understand the electrochemistry of the

ceramic material surface in aqueous suspension, rheological characterization of concentrated suspensions to understand how to control its flow behavior using polyelectrolyte-based dispersants, and characterization of mullite and chromia dip coatings on SiC substrates and chromia-based refractory brick, respectively.

EXPERIMENTAL PROCEDURE

Mullite, i.e., $3Al_2O_3$-$2SiO_2$, (MULCR®, Baikowski International Corporation, Charlotte, NC), three (3) commercial chromia refractory brick (CB) materials, and an ARC modified chromia based system were used as the ceramic powders in this study. The mullite powder was attritor milled to an average particle size of ~ 0.5 μm and surface area of 26.0 m^2/g, determined using dynamic light scattering (Zetasizer 3000HS, Malvern Instruments Ltd., Worcestershire, UK) and BET (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL), respectively. ARC provided ORNL all four (4) chromia based systems, and the materials were used in as-received form. Polyethylenimine (PEI), a cationic polyelectrolyte with a weight average molecular weight of 10,000 g/mole and one protonizable amine group (NH) per monomer unit was used as a rheological modifier for the mullite system. Due to reactivity of the chromia system in water, the dispersant, a poly(acrylic acid)-poly(ethylene oxide) (PAA-PEO) copolymer (Advaflow®, Grace Construction Products, Cambridge MA) was used, which has been demonstrated to be effective for fine ceramic powders that react with water.[12] (Note, the average molecular weight was 5000 g/mole and 2000 g/mole for the PAA and PEO, respectively).

Zeta potential measurements were carried out on the chromia 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 (0.01 *M*) of varying pH ranging from 2 – 11. The solutions were adjusted to the appropriate pH using stock solutions of nitric acid or ammonium hydroxide. The suspensions were ultrasonically treated for 120 s to break up soft agglomerates prior to measurement.

Rheological measurements were carried out on concentrated mullite and chromia suspensions using a controlled-stress rheometer (Rheometric Scientific SR5, TA Instruments, New Castle, DE) fitted with concentric cylinder geometry. Concentrated mullite suspensions (45 vol% solids) were formulated by mixing an appropriate amount of mullite powder into aqueous solutions (pH 7) of varying PEI concentration. Chromia suspensions of varying solids loading were prepared by combining an appropriate amount of ceramic powder to aqueous solutions (pH 9) and varying PAA-PEO concentration. The suspensions were ultrasonically treated for 300 s to break up soft agglomerates, and then stirred for 24 hours to achieve equilibrium. Prior to measurement, the suspensions were presheared at a stress of 200 Pa for 300 s and then allowed to equilibrate for 900 s. Furthermore, 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 ramping an applied shear stress (logarithmically) from 0.025 to 200 Pa. A delay time (i.e., the time between two consecutive data acquisition events) of 60 s was used in this study.

Silicon carbide substrates (Hexaloy, Carborundum Co., Niagara Falls, NY) that were 20 mm x 6.5 mm x 6.5 mm in size were dipped into the concentrated mullite suspensions (45 vol%) of varying PEI concentration. The chromia refractory brick compositions (CB1, CB2, CB3 and ARC1) were cut into cubes of approximately 1 cm^3 in size. The cubes were subsequently inserted into concentrated chromia-based suspensions of comparable composition, e.g., the CB1 bricks were dipped into the CB1 slurries. All of the coated substrates were dried under ambient conditions, heat treated at 600°C to burn out any organic additions, and sintered at varying temperature and atmosphere (e.g., air, argon, and nitrogen)

RESULTS AND DISCUSSION

ZETA POTENTIAL

Zeta potential measurements were carried out on dilute chromia suspensions (10^{-3} vol% solids) of varying pH and the results are shown in Fig. 1. The isoelectric point (IEP) was observed at pH 4.6. In addition, at pH 9, the Cr_2O_3 particle surface underwent charge reversal and a sharp increased in zeta potential to 40 mV. This phenomenon may indicate the formation of a passive hydroxide layer on the surface of the Cr_2O_3 particles. The net positive surface potential at pH 9 indicates that an anionic polyelectrolyte (e.g., the PAA-PEO copolymer) that is fully (negatively) charged at these pH conditions will strongly adsorb to the surface of the particles. The adsorbed PAA-PEO, in turn, promotes dispersion of the particles. (Note, prior zeta potential measurements identified the cationic polyelectrolyte, PEI, as a good dispersant for the mullite system).[13]

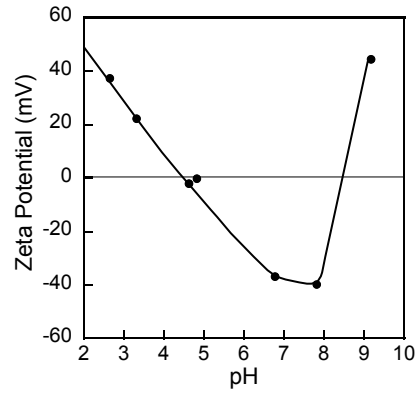


Fig. 1. Zeta potential as a function of pH for dilute chromia suspensions (10^{-3} vol% solids).

RHEOLOGICAL BEHAVIOR

Last year, mullite gels with slightly shear-thinning flow behavior were identified as the optimum rheological conditions for coating dense, silicon carbide substrates with mullite suspension. Porous refractory brick, on the other hand, is a much different surface and may not require the same conditions. Capillary forces that emerge from solvent wicking out of the coating layer into the porous brick aid to retain a uniform coating on the surface. In addition, the high surface roughness of the brick improves wetting. Thus, the particle gel network that serves to retain mullite slurries onto a nonporous substrate may not be necessary for chromia-based slurries on porous brick. For the latter, Newtonian flow behavior, indicative of a fully stabilized colloidal fluid may promote uniform coating, and perhaps, promote infiltration of the slurry into the porous brick.

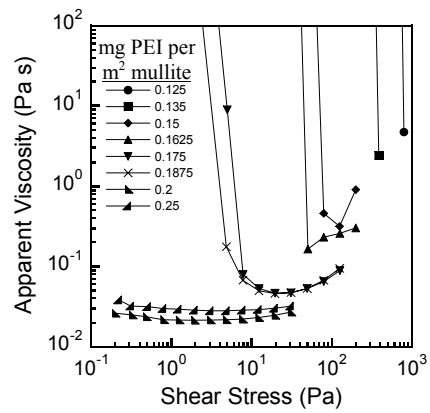


Fig. 2. Apparent viscosity as a function of shear stress for concentrated mullite suspensions (45 vol% solids) of varying PEI concentration.

Rheological measurements were carried out on concentrated mullite suspensions of varying PEI concentration as shown by the plot of apparent viscosity as a function of applied shear stress in Fig. 2. The degree of shear-thinning decreased with increasing PEI concentration until nearly Newtonian flow behavior was observed at 0.2 mg PEI/m^2 mullite.

The apparent viscosity is plotted as a function of applied shear stress in Fig. 3 for CB2 suspensions (a) of varying PAA-PEO concentration and (b) of varying solids loading. Strong shear-thinning flow behavior was observed in the absence of PAA-PEO dispersant; however, the degree of shear-thinning was reduced with the addition of PAA-PEO until a stable suspension, as indicated by Newtonian flow behavior, was observed at 0.1 mg PAA-PEO/g CB2 powder. Nearly Newtonian flow behavior was observed for suspensions with solids loading as high as 57.5 vol% in the presence of 1 mg PAA-PEO per g. CB2

powder. Similar flow behavior was observed for the other chromia-based systems at the high solids loading of 57.5 vol%, as shown in Fig. 4. High solids loading suspensions are required for the formation of dense, thick coatings on the refractory brick.

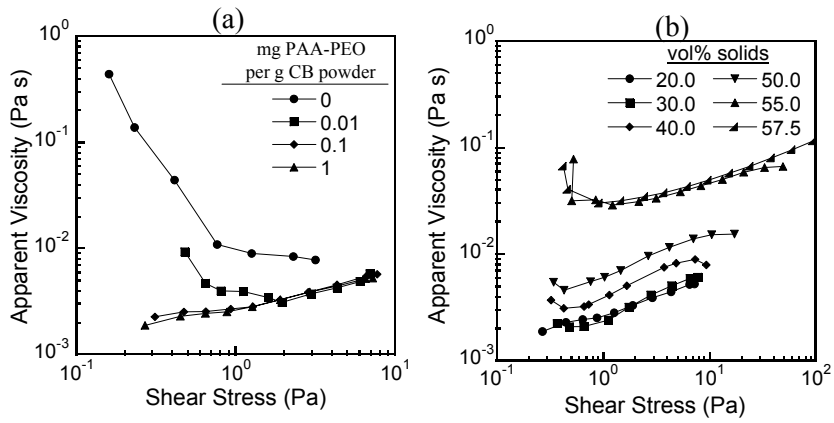


Fig. 3. Apparent viscosity as a function of shear stress for CB2 suspensions of (a) varying PAA-PEO addition (45 vol% solids) and (b) vary solids loading (1 mg PAA-PEO per g. CB1 powder).

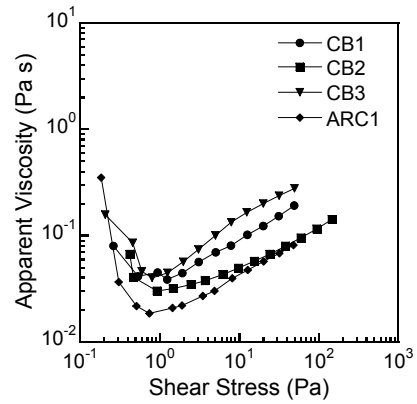


Fig. 4. Apparent viscosity as a function of shear stress for CB1, CB2, CB3, and ARC1 suspensions (57.5 vol% solids, 1 mg PAA-PEO per g. powder).

COATING FORMATION

Silicon carbide substrates were dipped into mullite suspensions (45 vol% solids) of varying rheological behavior and the resulting coatings are displayed in Fig. 5. Excellent coatings were obtained from mullite suspensions with slightly shear-thinning flow behavior obtained with the addition of 0.1625 - 0.175 mg PEI/m^2 mullite surface. Below this range, the coatings were thick and uneven, and cracks formed after drying. Above this range, uneven coatings were obtained because the slurry formed beads away from the corners and edges and flowed off of the substrate under the influence of gravity. By reducing the solids loading to 25 vol% and utilizing colloidal processing techniques to mimic the shear-thinning rheology of the more concentrated mullite suspensions discussed above (45 vol%), uniform layers of lesser thickness were formed by the dip-coating process.

0.15 **0.1625** **0.175** **0.1875** **0.20**

Fig. 5. Resultant coatings from dipping SiC substrates into concentrated mullite suspensions (45 vol%) of varying PEI concentration ranging between 0.15-0.20 mg PEI/m^2 mullite.

The chromia-based refractory brick "cubes" were inserted into Newtonian, chromia-based suspensions (57.5 vol%, 1 mg PAA-PEO per g. powder) with ceramic powder composition identical to the cubes. The resultant coatings deposited onto the brick are shown in Fig. 6. Our results confirm that chromia-based slurries with Newtonian flow behavior are sufficient to uniformly coat the porous brick.

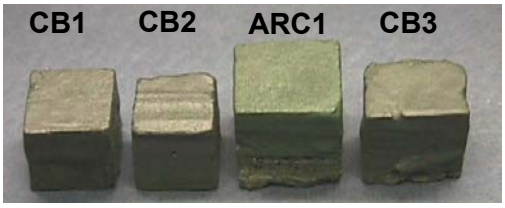
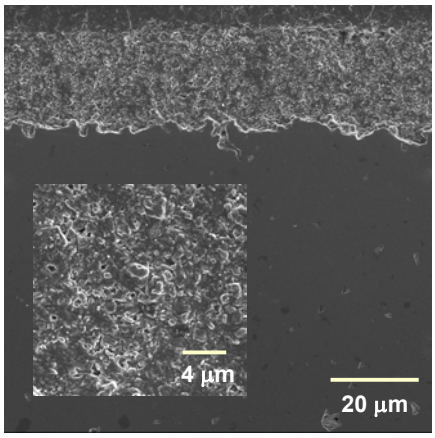


Fig. 6. Resultant coatings formed from dipping chromia-based brick into suspensions (57.5 vol% solids, 1 mg PAA-PEO per g. powder) of like composition. Note, the coating conformed uniformly to the CB2 brick, whose surface was rough compared to the other bricks shown here.

SINTERING BEHAVIOR

After sintering at 1400°C for 2 h in air (1 atm), a uniform, adherent mullite layer of ~ 20 μm thickness was obtained, as shown in Fig. 7. The presence of the mullite layer did not reduce the mechanical strength of the substrate, as determined by four-point bend tests of coated and uncoated bend bars. These early results are encouraging since the application of plasma sprayed coatings can significantly reduce the high temperature mechanical strength.[14] Although it is not apparent that there is interconnected porosity in the coatings, some silica was detected at the mullite/SiC interface after exposure to 1200°C steam for 500 h. Presumably, this reaction is a result of oxygen diffusion through pores in the coating; however, further iteration is necessary to qualify the density of the coatings required to protect the underlying substrate from fossil environments.



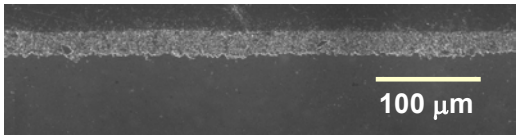


Fig. 7. SEM micrographs of a mullite layer on a SiC substrate. The layer was formed by dipping the substrate into a mullite suspension of 0.25 volume fraction solids, drying, and sintering at 1400°C for 2 h.

Micrographs of the chromia-based coatings are shown in Fig. 8 after sintering at 1600°C for 2 h in air (1 atm). Uniform layers, approximately 50-100 μm in thickness were obtained (note, the final, desired coating thickness will not be determined until corrosion testing can be completed). Furthermore, some of the slurry penetrated into the brick through the larger pores (~ 100 μm diameter). The coating density varied for the different systems, where the ARC composition was the densest of all the systems, and CB2 was the densest of the commercial brick systems. The coating density did not improve after sintering for longer times (12 h).

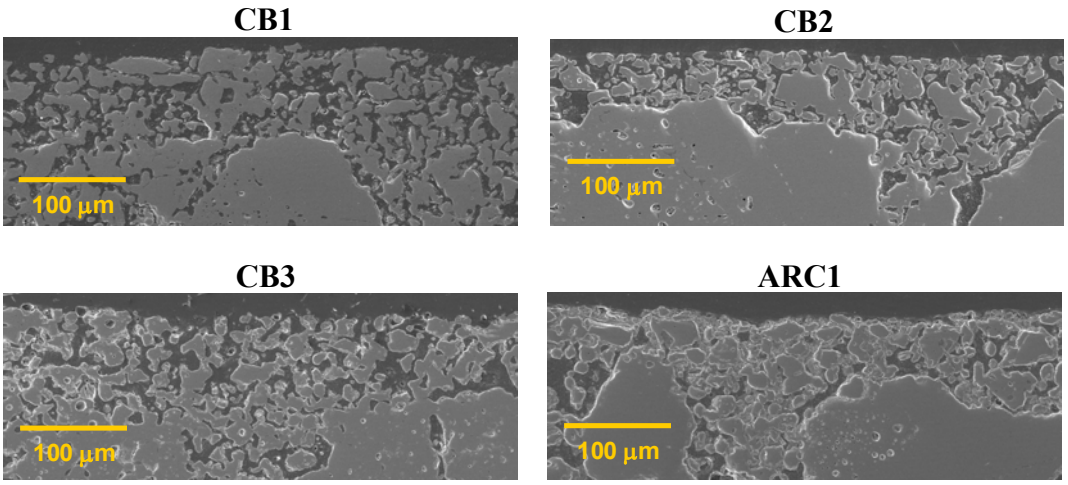


Fig. 8. SEM micrographs of chromia-based layers on refractory brick. The layers were formed by dipping the bricks into suspensions (57.5 vol%, 1 mg PAA-PEO per g. powder) of like composition to each respective brick. The coated bricks were dried and sintered at 1600°C in air.

The CB2 system was sintered in Ar (1 atm) for 2 h, and exhibited marked improvement in coating density as shown in Fig. 9. Furthermore, the coating density was improved after air sintering with the addition of a sintering aid (see Fig. 10). Initial coating studies are promising, thus the internal surface of chromia-based refractory cups will be coated for molten slag penetration tests to be performed at Albany Research Center.

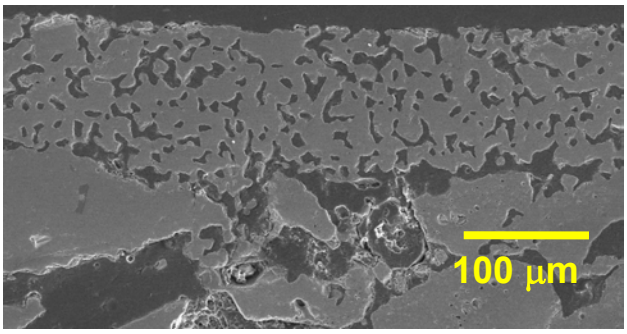


Fig. 9. A SEM micrograph of a CB2 coating on CB2 refractory brick. The layer was formed by dipping a CB2 brick into a suspension (57.5 vol%, 1 mg PAA-PEO per g. powder) of like composition. The coated brick was dried and sintered at 1600°C in Ar.

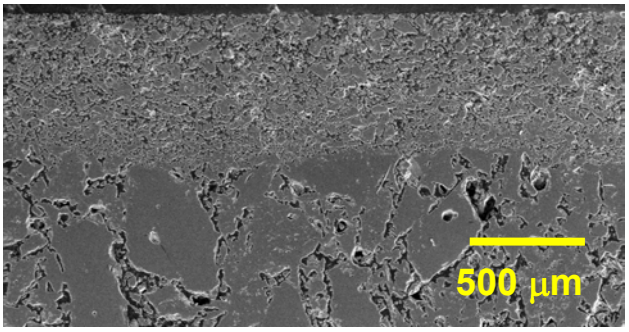


Fig. 10. A SEM micrograph of a CB2 coating on CB2 refractory brick. The layer was formed by dipping the brick into a suspension (57.5 vol%, 1 mg PAA-PEO per g. powder) of like composition to the brick, with the exception of a sintering aide. This addition also promoted slightly shear-thinning flow behavior, resulting in increased coating thickness. The coated brick was dried and sintered at 1600°C in air.

CONCLUSIONS

The ORNL slurry coating approach is a low-cost method to deposit protective layers on SiC ceramics and chromia-based refractory brick for use in fossil energy applications. The surface of chromia particles in aqueous suspension was characterized using zeta potential measurements. Polyelectrolyte dispersants were identified to modify the rheological behavior of concentrated mullite and chromia-based suspensions. Slightly shear thinning and nearly Newtonian flow behavior was identified as the optimal slurry rheology needed to coat nonporous SiC and porous, chromia-based refractory brick, respectively. Sintering conditions have been explored to densify the coatings, and ongoing, iterative efforts are underway to maximize the properties of the systems in their respective environments.

ACKNOWLEDGMENTS

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