CORROSION RESISTANT CERAMIC COATINGS: FORMATION OF MULLITE COATINGS ON SiC SUBSTRATES FROM COLLOIDAL SUSPENSION

Beth L. Armstrong
Oak Ridge National Laboratory
Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831-6063
Email: armstrongbl@ornl.gov; Telephone: (865) 241-5862; Fax: (865) 574-6918

Glen H. Kirby
Oak Ridge National Laboratory
Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831-6063
Email: kirbygh@ornl.gov; Telephone: (865) 576-6545; Fax: (865) 574-6918

Kevin M. Cooley
Oak Ridge National Laboratory
Bethel Valley Road, P.O. Box 2008, Oak Ridge, TN 37831-6063
Email: cooleykm@ornl.gov; Telephone: (865) 574-4559; Fax: (865) 574-6918

INTRODUCTION

Advanced fossil energy processes have hostile environments with temperatures as high as 1400°C and atmospheres that contain water vapor, sulfur, nitrogen, trace heavy metals, and alkali salts. Silicon-based ceramics such as SiC or SiC/SiC composites are attractive for use in these 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 or the development of material with improved stability in these harsh environments is necessary.

Colloidal processing of ceramic suspensions offers a low-cost alternative approach for producing uniform, thick ceramic coatings on complex-shaped components via a simple dip 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 interparticle forces.[4,5]

In this study, concentrated, aqueous suspensions comprised of mullite particles are developed for use in a dip-coating process. Mullite is chosen to demonstrate the feasibility of this process as its behavior is well-characterized in fossil environments. The approach consists of zeta potential measurements as a function of pH to understand the electrochemistry of mullite surfaces in aqueous suspension, rheological characterization of concentrated suspensions to understand the influence of a polyelectrolyte (polyethylenimine) on the bulk suspension properties, and characterization of green and sintered mullite dip coatings on SiC substrates.

DISCUSSION OF CURRENT ACTIVITIES

MATERIALS SYSTEM

Mullite, i.e., $3Al_2O_3{\cdot}2SiO_2$, (MULCR®, Baikowski International Corporation, Charlotte, NC) was used as the ceramic powder in this study. The mullite powder was attritor milled to an average particle size of 1 μm and surface area of 26.0 m^2/g, determined using dynamic light scattering (LA-700, Horiba Instruments Incorporated, Irvine, CA) and BET (Autosorb-1, Quantachrome Instruments, Boynton Beach, FL), respectively. Polyethylenimine (PEI), a cationic polyelectrolyte with a weight average molecular weight of 10,000 g/mol and one protonizable amine group (NH) per monomer unit, was used as a rheological modifier. The fraction of protonated amine groups, α, was determined by potentiometric titration and is shown as a function of pH in Fig. 1 (Note, $\alpha = [NH_2^+]/([NH] + [NH_2^+])$).

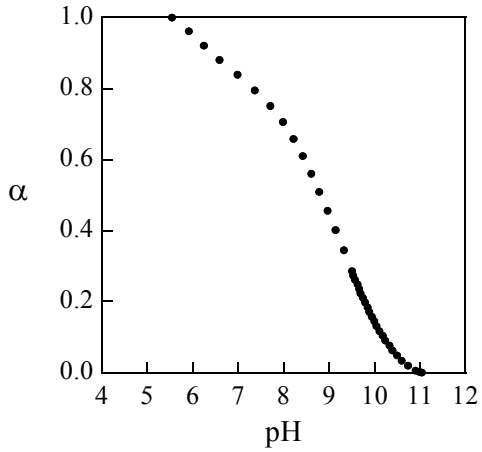


Fig. 1. Fraction of protonated amine groups, α, as a function of pH in dilute PEI solution (10^{-3} *M*). $\alpha = [NH_2^+]/([NH] + [NH_2^+])$.

ZETA POTENTIAL MEASUREMENTS

Zeta potential measurements were carried out on the mullite 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 2 min to break up soft agglomerates prior to measurement. A plot of the zeta potential as a function of suspension pH is shown in Fig. 2. Interestingly, the isoelectric point (IEP) was observed at pH 3.8, which is near the IEP reported for pure SiO_2 (pH 2-3) (ref. 6). Thus, favorable conditions for adsorption of PEI exist between pH 3.8 and 8.8 where the mullite particles are negatively charged and PEI is highly positively charged (i.e., $1 > \alpha > 0.5$).

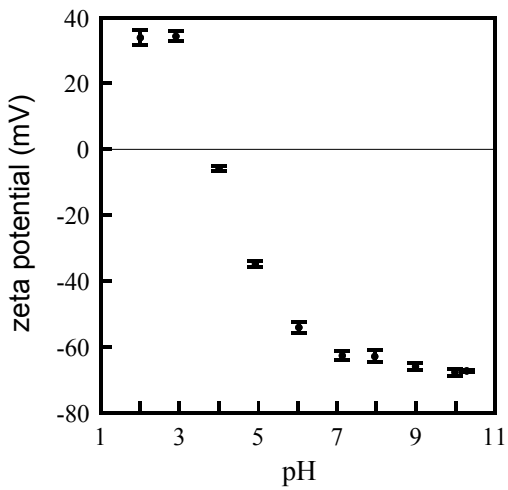


Fig. 2. Zeta potential as a function of pH for dilute mullite suspensions (10^{-3} vol% solids). Note, the data points and error bars represent the average and standard deviation, respectively, of ten measurements.

RHEOLOGICAL CHARACTERIZATION

Rheological measurements were carried out on concentrated mullite 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. The suspensions were ultrasonically treated for 5 min to break up soft agglomerates, then stirred for 24 hours to achieve equilibrium. Prior to measurement, the suspensions were presheared at a stress of 200 Pa for 5 min and then allowed to equilibrate for 15 min. Furthermore, a specially designed 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 1 min was used in this study. After repeating the preshear procedure mentioned above, storage modulus (G') measurements were carried out by ramping an

oscillatory shear stress (logarithmically) from 0.025 to 200 Pa at a constant frequency of 1 Hz. All rheological measurements were performed at a constant temperature of 25°C.

The results from the rheological measurements are shown in Figs. 3-5. The apparent viscosity is plotted as a function of applied shear stress in Fig. 3 for suspensions of varying PEI concentration. 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. These suspensions exhibited stable flow behavior over a 15-day time span, as shown by the results in Fig. 4. The elastic modulus is plotted as a function of applied shear stress in Fig. 5 for suspensions of varying PEI concentration. Solid-like behavior, indicative of colloidal gels, was observed for suspensions with less than 0.2 mg PEI/m^2 mullite. The linear elastic modulus and yield stress decreased with increasing PEI concentration until the transition from gel- to fluid-like behavior occurred at 0.2 mg PEI/m^2 mullite.

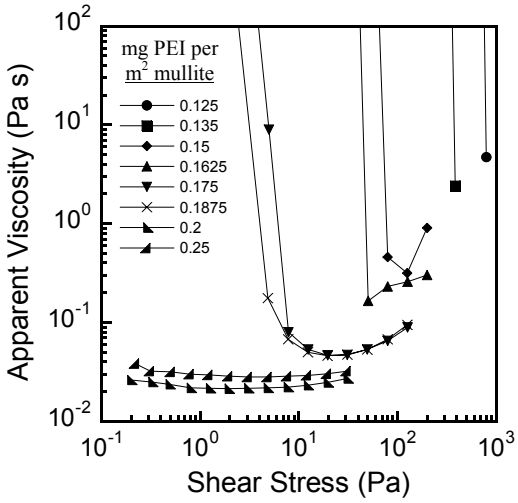


Fig. 3. Apparent viscosity as a function of shear stress for concentrated mullite suspensions (45 vol% solids) of varying PEI concentration. Note, the solid lines merely guide the eye.

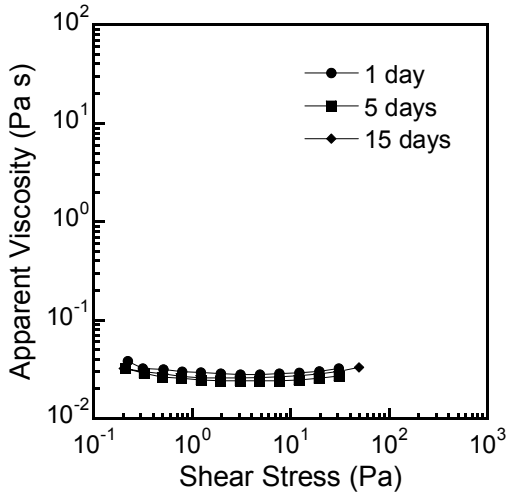


Fig. 4. Apparent viscosity as a function of shear stress for concentrated mullite suspensions (45 vol% solids, 0.25 mg PEI/m^2 mullite) aged for varying times.

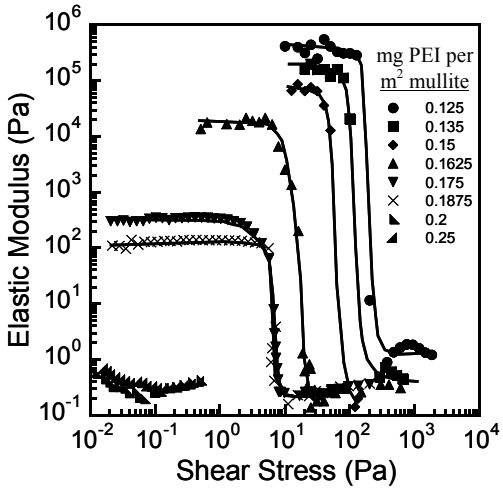
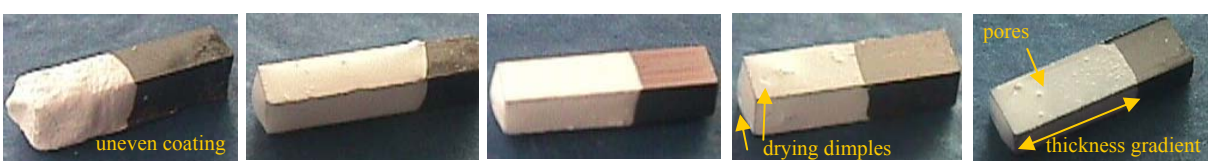


Fig. 5. Elastic modulus as a function of shear stress for concentrated mullite suspensions (45 vol% solids) of varying PEI concentration. Note, the solid lines merely guide the eye.

COATING FORMATION

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 substrates were inserted at a rate of 1.4 mm/s, submerged for 60 s, and withdrawn at a rate of 1.4 mm/s. The coated substrates were dried under ambient conditions, heat treated at 600°C to burn out any organics, and sintered at varying temperature and atmosphere (e.g., air, argon, and nitrogen). A gallery of the resulting coatings is displayed in Fig. 6. Excellent coatings were obtained from mullite suspensions with 0.1625 - 0.175 mg PEI/m^2 mullite surface. Mullite suspensions with less than 0.1625 mg PEI/m^2 mullite resulted in thick, uneven coatings that decreased in quality with decreasing PEI concentration. These features stem from a particle-gel network that is too strong, i.e., when the linear elastic modulus is greater than ~ 10 kPa. Mullite suspensions with 0.1875 mg PEI/m^2 mullite or greater resulted in coatings with three types of defects: thickness gradients, pores, and "dimples". These defects stem from a particle gel network that is too weak, i.e., when the linear elastic modulus is less than ~ 100 Pa. For example, thickness gradients result from dripping and beading of the suspensions at the bottom of the substrate. Pores arise from entrained air bubbles in the suspension, possibly stabilized by PEI, that quickly migrate through a liquid-like medium to the suspension/substrate interface during dipping. After drying, the air bubbles become locked into position at the interface to create the defect. Dimple-shaped defects form during drying in a process described by Martinez and Lewis.[7] Drying begins with fast evaporation of solvent at the corners and edges of a ceramic coating, but over time, the drying front converges inward until the center of the coating is completely dry. Concurrently, solvent wicks from the region of high solvent concentration (the center) to the region of low concentration (the drying front). If the gel structure is too weak, particles migrate with the fluid flow and ultimately, a dimple-shaped defect forms in the center of the coating.



0.15 0.1625 0.175 0.1875 0.20

Fig. 6. 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.

SINTERING BEHAVIOR

The sintering conditions, i.e., atmosphere and temperature, strongly influenced the ultimate coating quality. Dramatic differences were observed in the adherence of coatings depending on the sintering atmosphere. Adherent coatings were obtained in air, likely because a thin, silica-rich reaction layer formed to provide bonding. On the other hand, the coatings sintered in argon

and nitrogen atmospheres easily detached from the SiC substrates because a bond layer does not form. Furthermore, mullite and nitrogen likely reacted to form AlN, which could result in coating expansion and spallation.

Dense, adherent, macro crack-free coatings were obtained after sintering at 1350°C in air, as shown in Fig. 7. This temperature was significantly lower than the requirement for densification of bulk mullite (1600°C) (ref. 8) and was only slightly higher than the target operating temperature in fossil environments (~1200°C). The coating thickness varied from a few micrometers at the corners to ~ 150 μm at the midpoint of each edge. Future steps to optimize the suspension solids loading and the sintering conditions will be employed to minimize this thickness gradient.

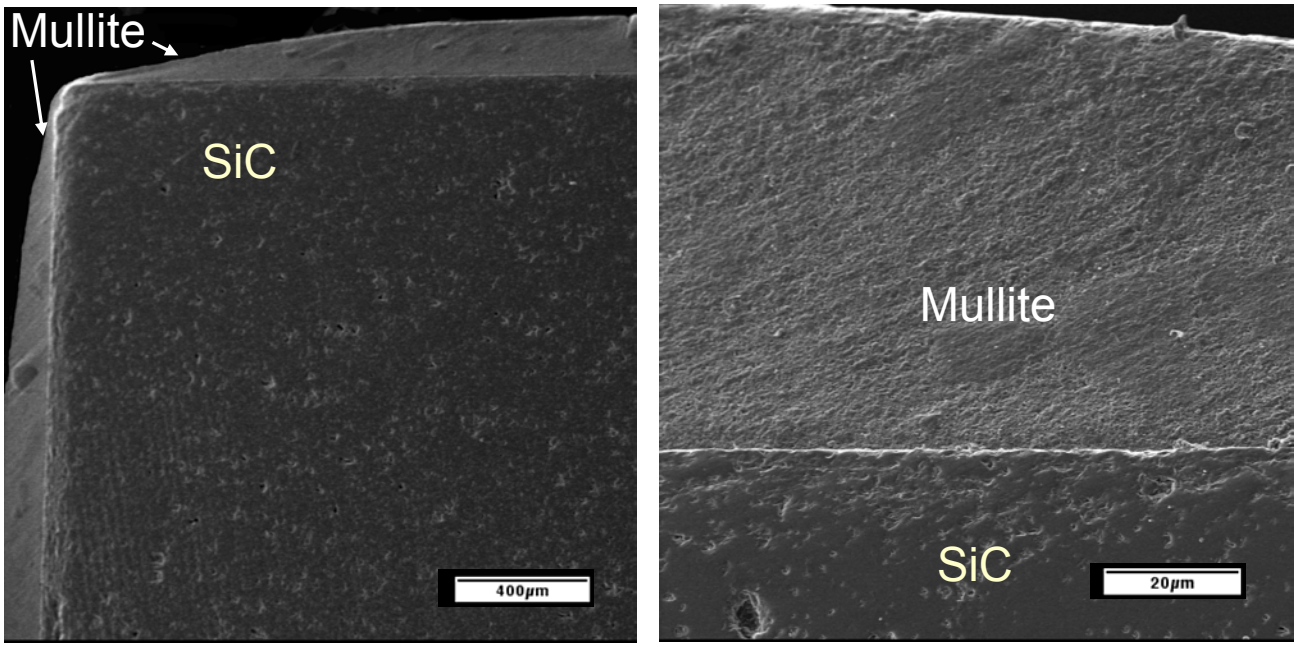


Fig. 7. SEM micrographs of mullite coated SiC, dipped from concentrated suspension precursors (45 vol% solids) with 0.175 mg PEI/m^2 mullte and sintered at 1350°C.

CONCLUSIONS

Dip coating is a feasible, low-cost method to coat SiC ceramics for use in fossil energy applications using concentrated, aqueous suspensions prepared via a colloidal processing approach. The surface of mullite particles in aqueous suspension was characterized using zeta potential measurements and PEI was identified as an effective additive to modify the particle surfaces to facilitate fabrication of concentrated colloidal suspensions. Rheological measurements indicated that fluids and gels of varying linear elastic modulus and yield stress can be tailored by varying the PEI concentration. The optimal PEI concentration for dip coating

ranged from 0.1625 - 0.175 mg PEI/m^2 mullite surface area. Dense, adherent, and macro crack-free mullite coatings were obtained on the SiC substrates after sintering at 1350°C in air.

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