

Corrosion Resistant Coatings for Ceramics

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Introduction

Silicon based ceramics such as silicon carbide (SiC) are attractive for use in hot-gas filters, heat exchangers, and other devices for advanced energy producing systems due to their higher temperature capability relative to metals, high thermal conductivity, retention of mechanical properties at operating temperatures, and excellent thermal shock resistance. Typically, a slow growing, silica scale protects the SiC material. This scale limits oxygen diffusion and thus prevents further attack of the substrate. A major drawback of SiC ceramics is the susceptibility of the silica scale to volatilization and corrosion by alkali salts such as Na_2SiO_4 and steam at high temperatures, which limits the applicability for extended service in many fossil energy conversion and combustion system environments. Thus, the use of protective coatings or the development of material with improved stability in these harsh environments becomes necessary. To address this issue, the development of novel coatings for SiC ceramics utilizing low-cost aqueous based processing methods such as screen-printing and dip coating is being pursued. Mullite was deposited on to SiC substrates and was evaluated for feasibility, specifically the thickness, density, microstructure and stability of the coating. Additionally, a processing approach is being developed for materials that form other types of protective scales such as the direct conversion of metal coatings to form alumina scales. Interim results for all of these approaches will be discussed.

The purpose of this program is to develop ceramic coatings with enhanced corrosion resistance through improvements in the composition and processing. Processing innovations will focus on aqueous coating development including such techniques as spray coating, screen-printing, and dip coating. In addition, materials that form scales other than silica will be evaluated. Candidate materials will be exposed in facilities at ORNL and will be characterized to identify the most promising materials for specific applications.

Slurry Coating Development

This program has been investigating several approaches to improving the environmental stability of SiC. One approach that is being taken is to coat the surface of a hexaloy SiC (SASiC) substrate using low cost, slurry based coatings. There are numerous slurry-based approaches including dip coating, screen-printing, spin coating, spray coating, and vacuum coating. All processes have indicative advantages and challenges, and these are summarized in Table 1. As a result, two coating methods were selected for evaluation; a near term, materials evaluation approach, screen-printing, and a long term, system evaluation approach, dip coating. Screen-printing was selected such that the candidate material systems could be quickly “screened” for efficacy while minimizing processing set-up times and parameters. Once the material issues are evaluated, development of a dip coating system will be initiated to demonstrate processing feasibility. The candidate material system, mullite, was selected based on thermal expansion match to SiC and relative corrosion resistance to fossil environments.

Table 1

Technique	Advantages	Issues
Dip Coating *	Inexpensive. Conducive to 3D structures.	Thickness variation as a function of dip direction.
Screen Printing *	Controlled coating thicknesses and densities	Difficult to coat 3D structures.
Spin coating	Thin coating.	Difficult to coat 3D structures.
Spray Coating *	Inexpensive. Conducive to 3D structures.	Thickness variation. Line of sight.
Vacuum Infiltration	Can coat internal or weave type structures.	Viscosity of slurry/depth of slurry penetration.

Coatings of Washington Mills mullite were prepared using the screen-printing process. Screen-printed coatings of mullite were densified on to the surface of SiC substrates using traditional air sintering techniques. The resulting coatings varied in thickness from 9 microns to 150 microns depending upon processing conditions. The importance of the effect of processing on the resulting microstructure and ultimately the effectiveness of the coating is illustrated in Figure 1. The edge views shown in Figures 1A and B are of sintered coatings that were applied using screen-printing and spray coating, respectively. The screen-printed coating is thin (approximately

10 microns) and dense whereas the sprayed coating is much thicker (approximately 25 microns) to provide closed porosity.

A SiC sample with a coating of approximately 150 microns thick was tested at 1204°C for 500 hours in 100% humidity. Upon completion of the test, there was little evidence of the mullite coating in the central path of the gas stream. Some mullite remained at the sample edges. In the central areas, silica was found underneath a mixed layer of mullite grains in an alumino-silicate matrix. The oxidation was comparable to an uncoated surface. As a result, processing conditions are being adapted to increase the density of the coating (increasing the solids content of the ink), to densify in non-oxidizing conditions to minimize any oxygen present in the boundary layer, and to add dopants such as alumina to the mullite to tie up any residual silica that may be present.

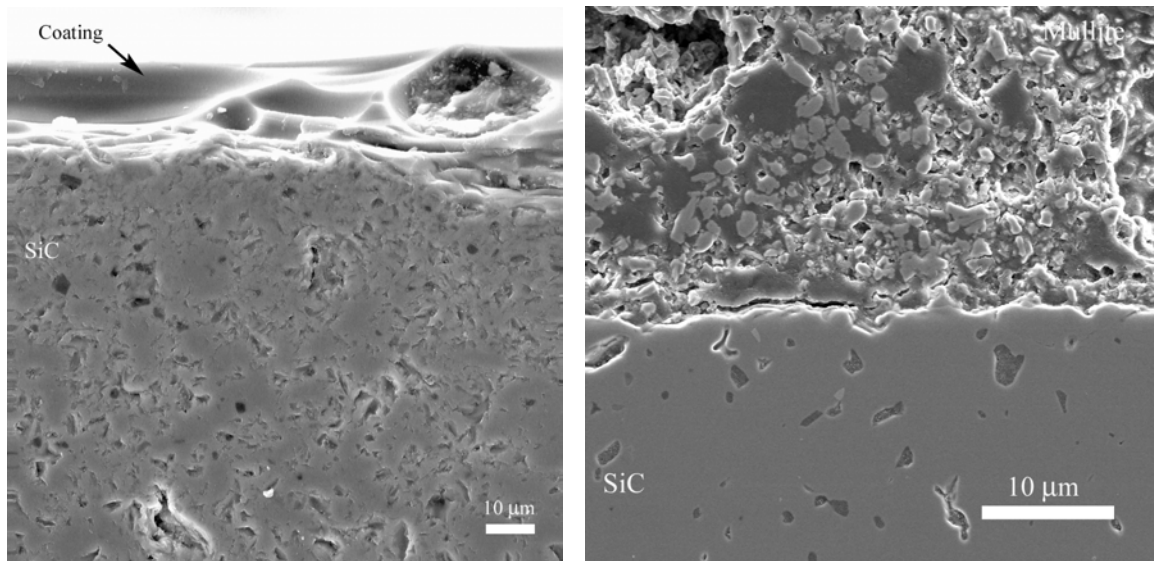


Figure 1. A) Mullite deposited by screen printing. Sintered at 1600°C in air for 2 hours. B) Mullite deposited by spraying. Sintered at 1600°C in air for 2 hours.

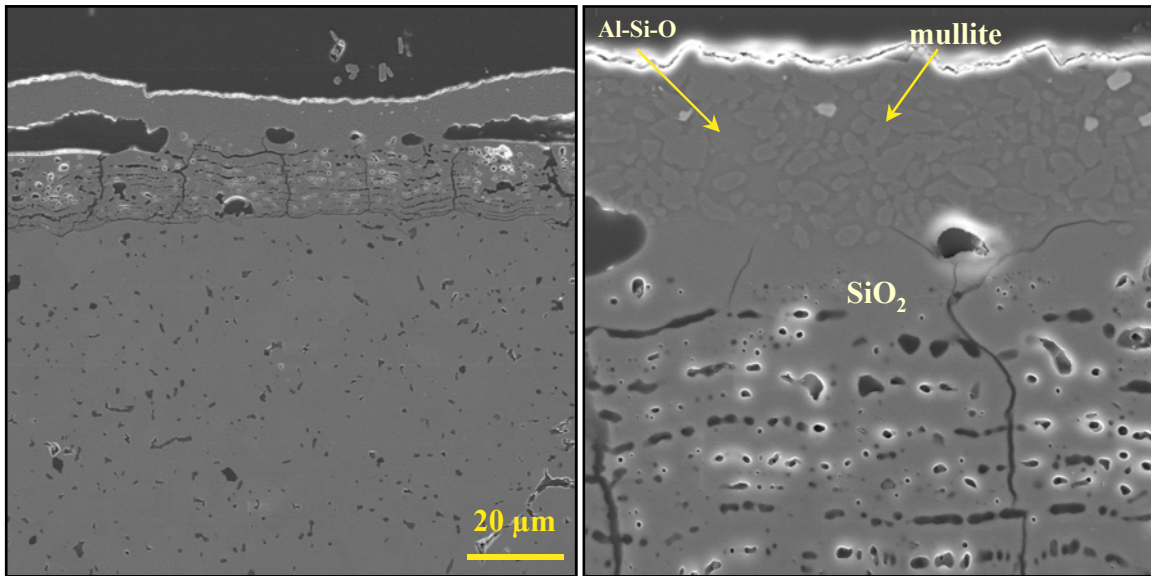


Figure 2. Polished Cross Section of Mullite Coating on SAlSiC After 500h Exposure at 1204°C, 100% H₂O

Surface Alloy Development Feasibility Study

One challenge in the densification of a slurry coating is the prevention of silica formation at the coating – substrate interface. Oxygen will diffuse to the substrate during the sintering process until densification is complete. Even if steps are taken to limit the oxygen diffusion during this densification process, the formation of a silica layer at the coating – substrate interface can still occur if the coating does not completely prevent oxygen transport. Thus, the development of a sacrificial coating that oxidizes and/or diffuses via a heat treatment or in-situ to form a volatility barrier have been proposed to address this concern. Thus, the concept of looking at the use of a thin metallic precursor layer as a route to form a self-graded oxide surface layers that can act as volatility barriers to protect against aggressive species that would degrade a silica layer was proposed. In this approach, the metal layer would completely convert to ceramic by an oxidation pretreatment.

For a feasibility evaluation, the authors proposed using five of the well characterized alumina-forming intermetallic systems, yttrium doped chrome aluminide (Cr₂AlY), titanium/yttrium doped chrome aluminide (TiCrAlY), hafnium doped nickel aluminide (NiAlHf), chromium/yttrium doped nickel aluminide (NiCrAlY), and chromium/yttrium doped iron aluminide (FeCrAlY). These compositions were selected with a range of CTE, high temperature strength properties in the metal layer, and base metal component chemistries in order to explore what the key issues are regarding the conversion of the metal layer to ceramic and the formation of a dense, adherent oxide after oxidation pretreatment. It is anticipated that the oxide layer formed will be a duplex layer with an outer layer of alumina and an inner layer consisting of a graded oxide layer of the base metal of the aluminide, Si and Al.

In order to determine if the concept of using thin metallic precursors was feasible, initial experiments used TiCrAlY coatings due to its low coefficient of thermal expansion (CTE) as compared to other alumina-forming materials. It was surmised that if this material would survive thermal cycling in laboratory air without spalling off the substrate, then further investigation of this approach was warranted. Feng Huang and Mark L. Weaver of the University of Alabama, Tuscaloosa sputtered a 2-3 micron coating of nominal composition Ti-51Al-12Cr (atom

percent) on to a SASiC substrate. The substrate was then exposed to ten, 100 hour cycles to 1100°C in laboratory air. Excellent adherence was seen as no spallation occurred. As shown in Figure 3, the alumina layer that formed at the surface was not continuous which indicated that the coating composition was not optimized. In spite of that, the excellent adherence that was demonstrated suggested that the concept of sacrificial metallic layers was worth more investigation.

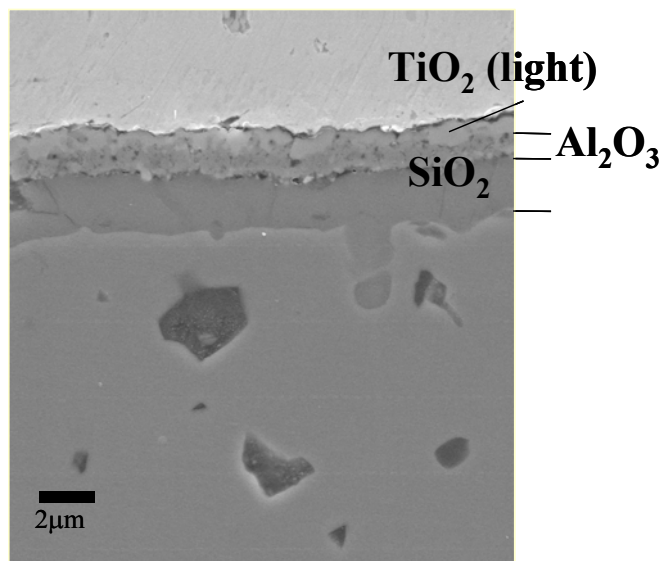


Figure 3. Exposure of 3 mm sputtered Ti-51Al-12Cr on SiC showed excellent adherence after ten, 100 hour cycles to 1100°C in laboratory air. No spallation occurred.

Coatings of NiAlHf, Cr_2AlY , NiCrAlY, and FeCrAlY were sputtered on to Hexaloy SASiC substrates for further investigation. The resulting substrates were exposed to 1150°C in flowing oxygen for 0.5 hour to convert the coating to alumina prior to stability testing. The resulting microstructures of the SASiC substrates exposed at 1150°C are shown in Figures 4 through 7. All of the coatings were adherent in spite of the thermal expansion coefficient mismatch from the starting materials. However, the full conversion to alpha alumina did not result from the chosen pretreatment. Raman spectroscopy showed evidence of transient alumina in all of the preheat-treated samples. The contribution of the coating and its interaction with the substrate can be noted in the different alumina morphologies produced after pretreatment as shown in Figures 4 through 7. Both the NiAl(Hf) and NiCrAlY coatings showed needle like morphology with some overall outer surface porosity. The Cr_2AlY and FeCrAlY had a more spherical morphology as expected with alpha alumina, but the overall outer density of the coating was still poor. The substrates were subsequently exposed to 72 hours at 1000°C in 100% humidity, and analysis is currently being completed. Modification of the pretreatment to eliminate transient alumina formation will be pursued.

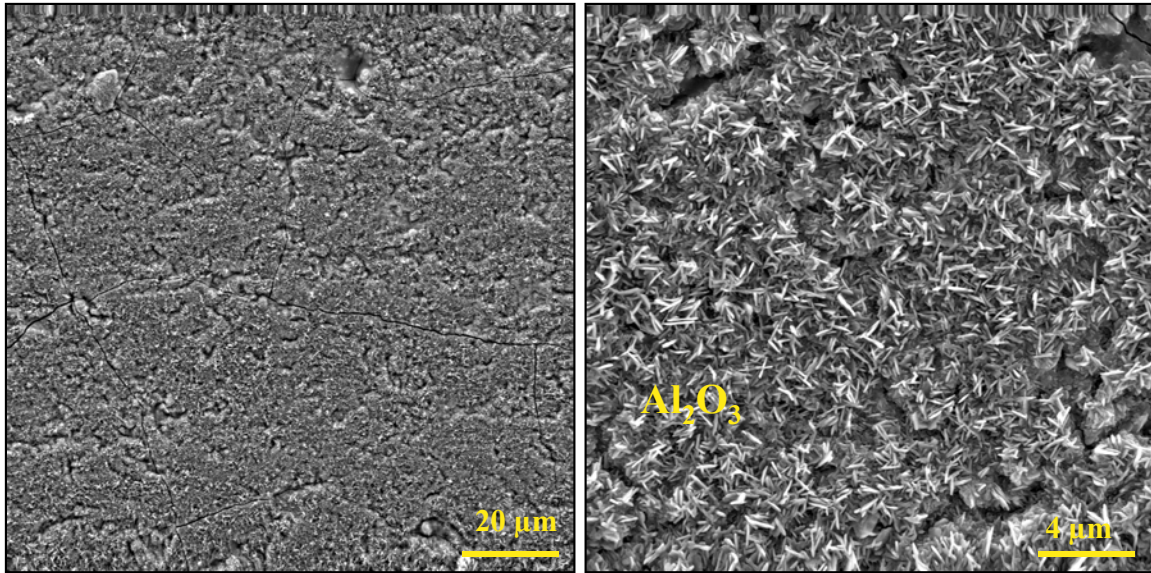


Figure 4. Surface Feature of NiAl(Hf) Coating on SASiC After 1150°C, 30 minute Heat Treatment

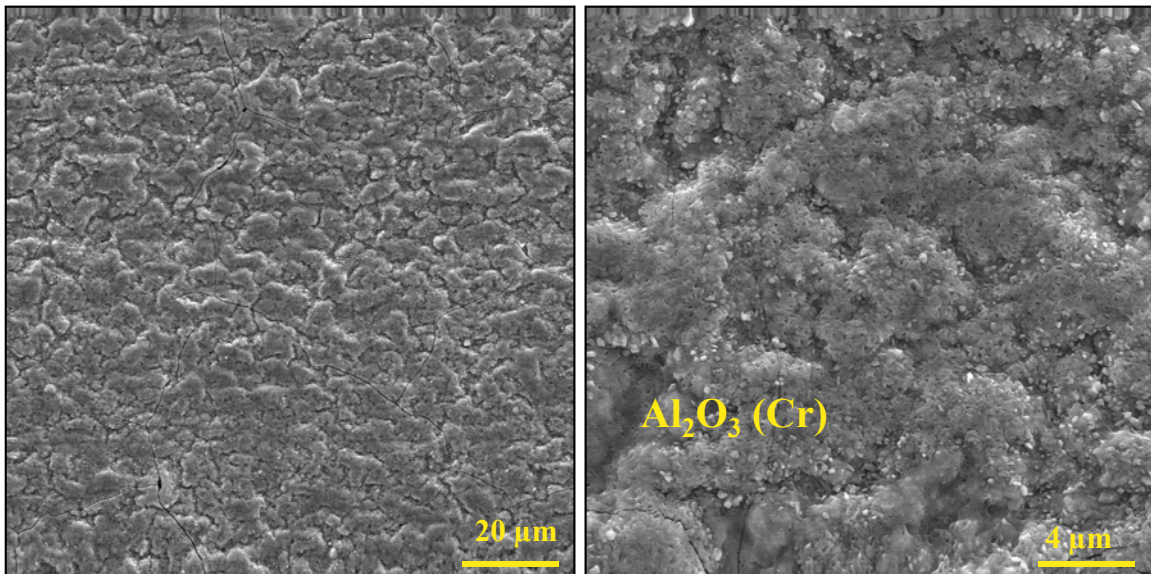


Figure 5. Surface Feature of Cr₂(Al)Y Coating on SASiC After 1150°C, 30 minute Heat Treatment

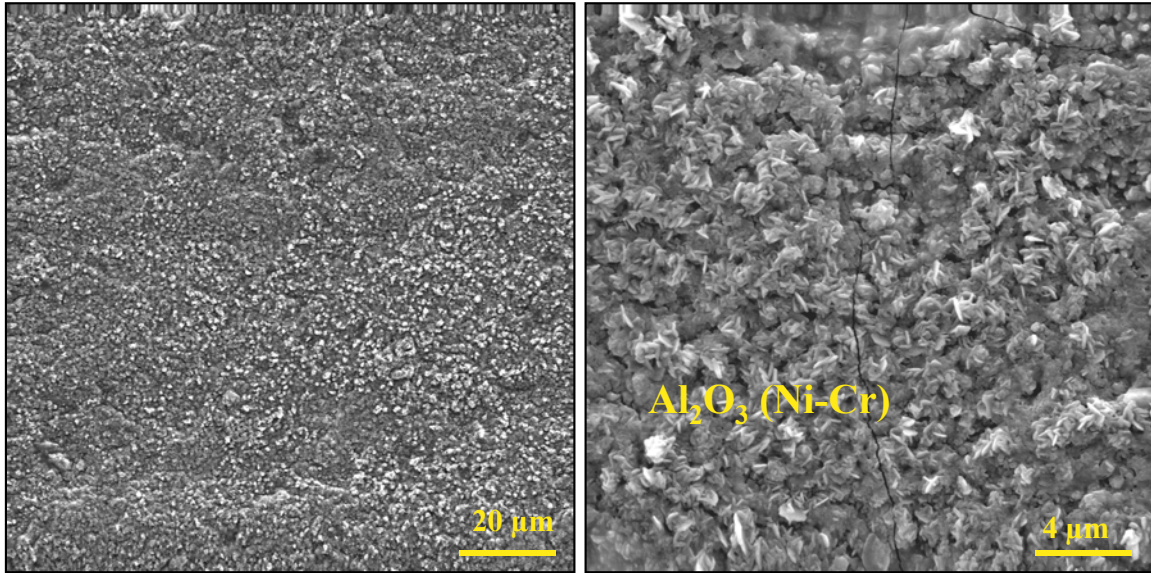


Figure 6. Surface Feature of NiCrAlY Coating on SASiC After 1150°C, 30 minute Heat Treatment

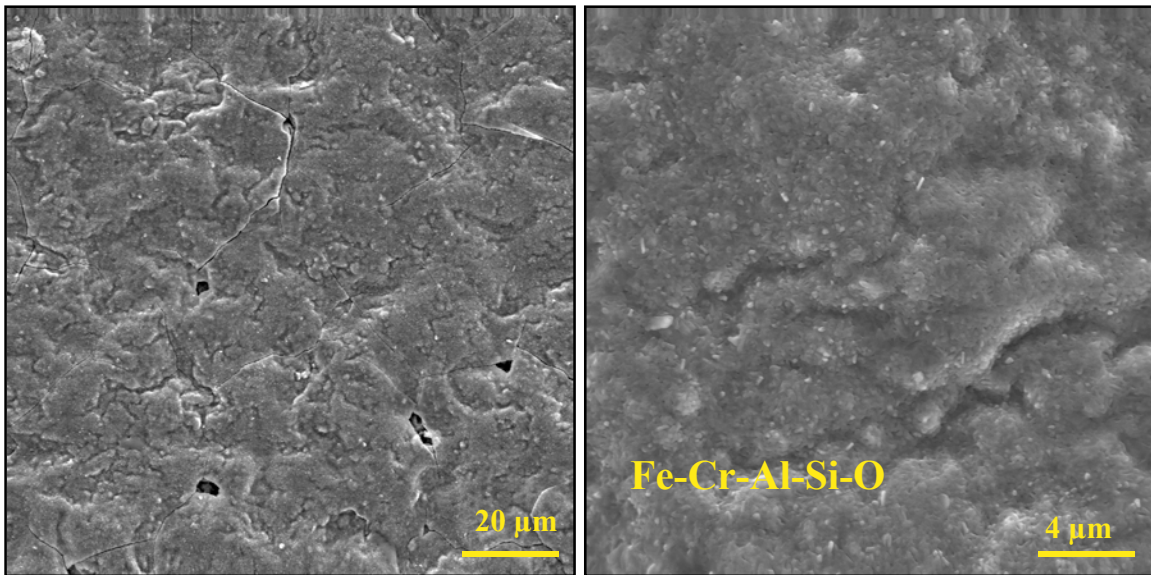


Figure 7. Surface Feature of FeCrAlY Coating on SASiC After 1150°C, 30 minute Heat Treatment

Summary

Two approaches were taken to address the development of novel, protective coatings for SiC ceramics for use in harsh fossil environments. The first approach utilized a low cost aqueous based slurry method. Screen-printed mullite coatings on SASiC substrates were tested at 1204°C for 500 hours in 100% water environment and demonstrated the feasibility of this process. The second approach that was proposed was a sacrificial coating that oxidizes via a heat treatment to form a volatility barrier. The feasibility of the concept was demonstrated using a thin metallic precursor layer. Four alumina-forming alloys were chosen and were tested first at 1150°C for 30 minutes in flowing oxygen and subsequently at 1000°C for 72 hours in 100% water environment.