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OXIDATION RESISTANT COATINGS FOR CERAMIC MATRIX COMPOSITE COMPONENTS

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ABSTRACT

Corrosion resistant $Ca_{0.6}Mg_{0.4}Zr_4(PO_4)_6$ (CMZP) and $Ca_{0.5}Sr_{0.5}Zr_4(PO_4)_6$ (CS-50) coatings for fiber-reinforced SiC-matrix composite heat exchanger tubes have been developed. Aqueous slurries of both oxides were prepared with high solids loading. One coating process consisted of dipping the samples in a slip. A tape casting process has also been created that produced relatively thin and dense coatings covering a large area. A processing technique was developed, utilizing a pre-sintering step, which produced coatings with minimal cracking.

INTRODUCTION

The necessity of operating in a high temperature and highly corrosive environment will require the use of ceramic materials in many fossil energy applications. Unfortunately, monolithic ceramics are brittle and exhibit very low toughness. These undesirable features limit the reliability, damage tolerance, and durability of monolithics and make them unsuitable for many fossil energy applications. Emphasis has thus been placed on the development of ceramic matrices reinforced with strong ceramic fibers. Such ceramic matrix composites (CMC's) combine the temperature stability of monolithic ceramics with the "graceful" failure of fiber reinforced composites.

The corrosion of silicon carbide based fibers and matrix materials in the presence of alkali species[1,2] is a major problem in certain fossil energy applications, such as hot-gas filters and heat exchangers. The alkali species, mainly sodium compounds, are by-products from the combustion of fossil fuels. Therefore, corrosion/oxidation resistant coatings for the exterior of CMC components are needed for durability and reliability in such environments.

Thirty years ago, a new family of ceramic materials was developed based on the crystal structure of sodium zirconium phosphate $NaZr_2(PO_4)_3$ (NZP).[3,4] $Ca_{0.6}Mg_{0.4}Zr_4(PO_4)_6$ (CMZP)[5] and $Ca_{0.5}Sr_{0.5}Zr_4(PO_4)_6$ (CS-50)[6] have been derived from this family and possess a near-zero thermal expansion coefficient, low thermal conductivity and good thermal stability up to 1500°C which make them excellent candidates for high temperature applications. Additionally, these oxides have shown great promise for operating in an alkali environment. CMZP coatings produced by sol-gel techniques on silicon carbide and silicon nitride have provided protection to alkali exposure at 1000°C.[7,8,9] The interaction between plasma-sprayed CS-50 coatings, as well as bulk CS-50, and sodium sulfite at high temperature has been studied, and CS-50 remained unaffected after alkali exposure.[10,11] The goal of this study is to develop a protective coating of these two NZP formulations. Processing techniques focused on two cost-effective, water-based slurry-coating methods: A slurry dipping process and a tape-casting process.

EXPERIMENTAL PROCEDURE

Substrate Preparation

Ceramic grade Nicalon™ fiber-reinforced SiC matrix composites prepared by chemical vapor infiltration by the Ceramic Surface Systems Group at Oak Ridge National Laboratory (ORNL) were used in this study. Flat samples as well as ring samples cut from prototypical heat exchanger tubes were machined to the appropriate size.

The fibers and woven pattern of the composite offer a very textured surface that provides good interlocking sites for the coating. To further improve the infiltration of the slurry into crevices in the composite, the effort focused on improving the wettability of the substrate by the slurry. The impact of an intermediate oxide layer on substrate wettability was evaluated. A first oxidation process was assessed which consisted of heating the specimens to 1000° C for four hours. The second process was developed by Li et al.[8] and involves a chemical route. The substrates were washed in acetone, dried, washed in HF, rinsed, dried, calcined at 1200°C, washed in HCl and finally rinsed and dried. The wettability of untreated and oxidized monolithic SiC was then measured with water in an environmental chamber. Surface oxidation of monolithic SiC improved its wettability since contact measurements were ~55° for untreated samples and ~40° for oxidized specimen. In order to reduce the use of harmful chemicals in the coating process, the thermal oxidation process was chosen over the chemical oxidation process. Additionally, some samples presenting large smooth areas where most of the fibers were completely embedded in the matrix exhibited poor coating adhesion. Roughening of the surface with 60-grit sandpaper before oxidation improved coating adherence of these samples.

Powder and Slip Preparation

Powder Preparation

CMZP powder was prepared at Virginia Polytechnic Institute and State University and New Mexico Institute of Mining and Technology by a proprietary method and was screened to 100-mesh. The powder was then fully crystallized by heating it to 1200°C for 4 h. CS-50 powder was obtained from LoTEC Inc. (Salt Lake City, UT). The powder was fully calcined with an initial average particle size of 10 μm.

Particle size distribution is important and must be optimized to obtain a high quality coating. A small and narrow particle size distribution allows higher solids loading, thus milling trials were performed to optimize powder size and distribution. The desired particle size and distribution was reached after 48 h of wet milling with a pearled zirconia media. Particle size analysis was completed using a Horiba LA-700 particle size analyzer. A mean particle size of ~0.9 μm was obtained for CS-50 and CMZP. The particle size distribution was very narrow with a standard deviation of 0.25 μm for both powders.

Slip Composition

A proprietary CMZP slip composition was adjusted to obtain the best rheology for dip coating. Dolapix PC 21 (Zschimmer and Schwartz, Lahnstein Germany) replaced the original dispersant. A CS-50 slurry was also prepared according to a proprietary composition. The powder was gradually added to the slurry to obtain the maximum powder-to-water ratio. Maximizing the solids loading will increase contact between particles and reduce the amount of water which must be removed during drying. A solids loading of 33 vol% was initially used for coatings with a goal of reaching 55 to 60 vol% solids loading. Currently, a solids loading of 60 vol% was obtained for CMZP and 63 vol% for CS-50. The binder content of the slurries was then modified according to the coating technology. Dipping required a low viscosity slurry to obtain thin coatings and no binder was added to the dispersant. Tape casting required a thicker, more plastic slurry obtained with the addition of binders, Methocel (Dow Corning, Midland, MI) or polyvinyl alcohol (PVA, grade 75-15, Dupont, Wilmington, DE), and plasticizers such as polyethylene glycol (PEG, ME Science, Gibbstown, NJ). The gel-like slurry was easily sprayed on the substrate and the casting process was improved.

ZnO (ME Science) was added to both slurries as a sintering aid. The effect of ZnO on the sintering behavior of NZP materials has been found to create a liquid phase which promotes the sintering reaction[12,5,13]. In CMZP, Ca^{2+} and Mg^{2+} dissolve in a liquid phase of $Zn_3(PO_4)_6$ that forms at 1000°C. In order to reduce coating cracking during densification, it was believed that the coating should behave more like a glaze. Therefore, the amount of ZnO additions, as well as particle size and sintering temperature have been optimized to obtain the maximum of liquid phase. Aging of the slurry by milling proved detrimental to the coating quality. As the viscosity increased, the pH decreased causing the slurry to become less stable and to flocculate. Milling had to be limited to a maximum of 48 h.

Thermal Expansion Adjustment

Matching the coefficient of thermal expansion (CTE) of the coating to that of the substrate to prevent cracking and debonding, without detrimentally affecting the properties of the materials was investigated. Mixtures of CS-50 with a CTE of ~3.0x10-6/°C and 4% Y_2O_3 stabilized ZrO_2 (Tosoh Soda, Tokyo Japan) with a CTE of ~10x10-6/°C have been prepared to match the CTE of SiC ceramic matrix composites of ~4.5x10-6/°C[14]. Cold pressed samples of mixtures were prepared, sintered at 1300 °C for 8 h and analyzed by X-ray diffraction. No reaction between CMZP and 4 wt % Y_2O_3-stabilized ZrO_2 additive was found.

Coating application

Dip coating

Coatings were applied to composite rings by manually dipping the samples in the CMZP or CS-50 slurry. The samples were only dipped once since multiple dipping formed thick and non-uniform coatings which cracked in the thickest regions. It is anticipated that more controlled dipping of the samples will yield thinner, more uniform, higher quality coatings. Increasing withdrawal speed of the sample from the solution might also limit the formation of drops at the bottom of the specimen. Further improvements in the process will include mechanical dipping at varying rates.

Tape casting

The second slurry coating was obtained with a doctor-blade coating process also known as tape casting (Fig. 1). Tape casting is mostly used in the electronics industry.[15,16,17] This process was chosen for evaluation since it provides thin, large area and uniformly dense coatings. The use of a blade to level the coating allows an increase in the viscosity and the density of the slurry, which reduces shrinkage stresses. Additionally, coating thickness is precisely controlled (± 0.01 mm). The coating process is very simple and consists of covering the surface of the specimen with the slurry, leveling the coating with a doctor-blade, drying the specimen in a controlled environment and finally sintering the samples at a closely monitored rate. The quality of the coating is influenced by many different factors which were optimized as part of this program. Slurries were initially prepared as if for slip-casting then adjusted for tape casting. Low viscosity slurry flows off the substrate while a thick slurry cracks during processing.

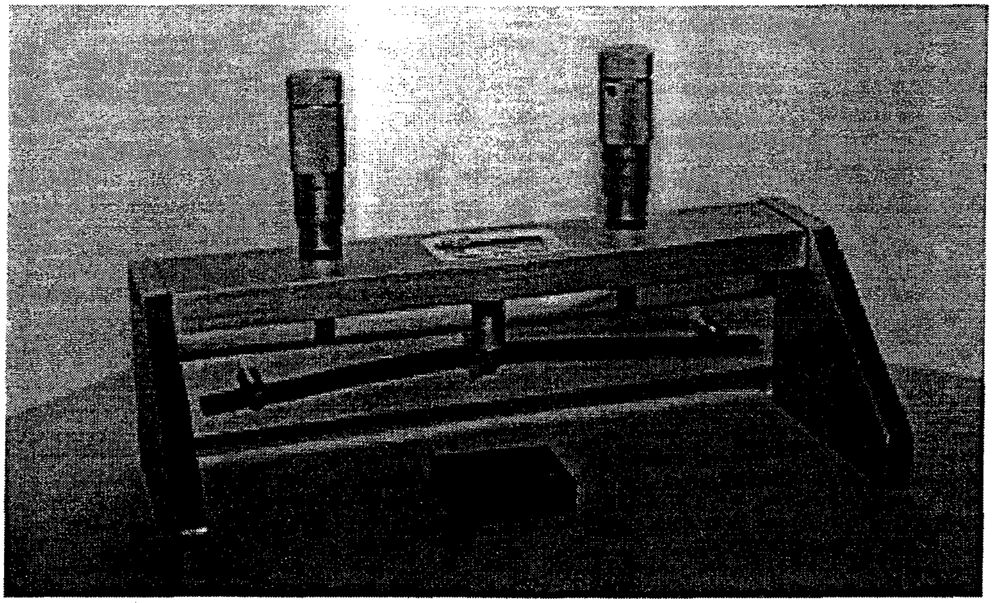

Figure 1: Doctor blade apparatus

Drying and sintering

After coating, the samples were kept at 80 % humidity for 48 h and then at ambient humidity for the same amount of time. The samples were then slowly heated at 0.5 °C/min up to 600 °C for 4 h to enable binder burnout. The samples were crack-free after this treatment. The specimens were then ramped at 1°C/min up to 1200°C, soaked for 1 min and cooled at the same rate down to room temperature. The same heating schedule was performed a second time, with a soaking time of 24 h at 1200°C. Stresses and deformations occurring during heating and cooling were minimized with the pre-sintering stage. A summary of the coating process is presented in Fig. 2.

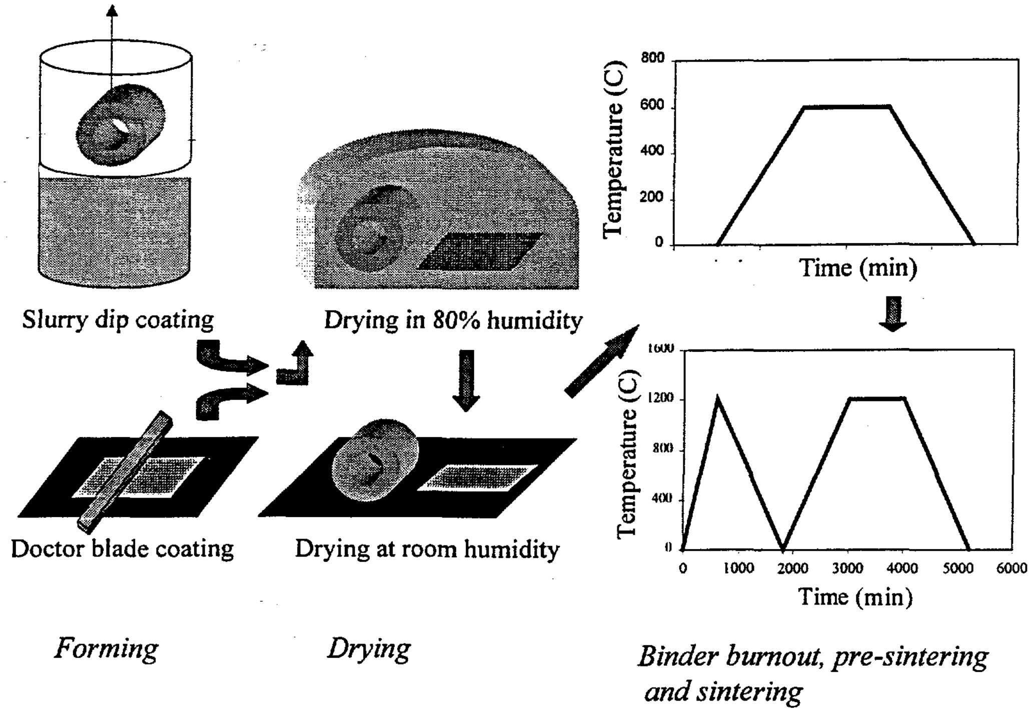

Figure 2: Coating deposition, drying and sintering process

Microscopy

Samples were embedded in epoxy resin, cut with a diamond saw and polished. Characterization of the coating/composite interface was first performed with an optical microscope, Nikon 4X, and then with a scanning electron microscope (SEM) Hitachi S800.

Corrosion Resistance of the Coatings

The surface of SiC oxidizes at high temperature to form a silica layer, which is responsible for the oxidation resistance of the material. There have been excellent reviews of the oxidation of SiC and Si_3N_4 which have shown that the protective silica layer, when in contact with molten sodium salts, reacts to form a sodium silicate liquid, resulting in an increase in the oxidation rate[1,2]. Several types of corrosion studies have been evaluated; (a) burner rig corrosion test,[18] (b) application of a thin film of sodium sulfite or sodium carbonate and heating the coated specimen to the desired temperature,[19] (c) partial or complete immersion of the specimen in a crucible containing the alkali melt. A thin film procedure was performed for this evaluation. A total of five specimens were used; two coated with CS-50, one coated with CMZP and two reference composites. The dimensions of the samples were carefully measured and the specimens were weighed. Then the specimens were washed in an ultrasonic cleaner in acetone followed by distilled water. The samples were dried overnight in an oven at 60°C. The sodium sulfate loading was performed by heating the specimen on a hot plate to 90°C and dispensing drops of saturated Na_2SO_4 solution onto the surface. The samples were left to dry for an hour, weighed and more sodium sulfate was added until the loading reached 8 mg/cm^2. The samples were then heated in a furnace to 1000°C for 100 h in flowing O_2 (200 cm^3/min). The specimens were then weighed, washed in hot distilled water for two hours to dissolve any residual sodium sulfate and then weighed again. Phases present on the sample surface were determined before and after corrosion by standard XRD. Some samples were then cut, polished using kerosene as a lubricant and viewed with the SEM to determine any microstructural changes. Energy dispersive X-ray analysis (EDX) was also used to evaluate the penetration depth of sodium compounds.

RESULTS

Visual Evaluation

Good quality coatings exhibiting few cracks and a smooth surface were obtained and are illustrated in Fig. 3 and 4.

ZnO additions were beneficial to the coating quality as seen in Fig. 5. Because of the liquid phase present, the coating flowed around the substrate and was less likely to crack during densification.

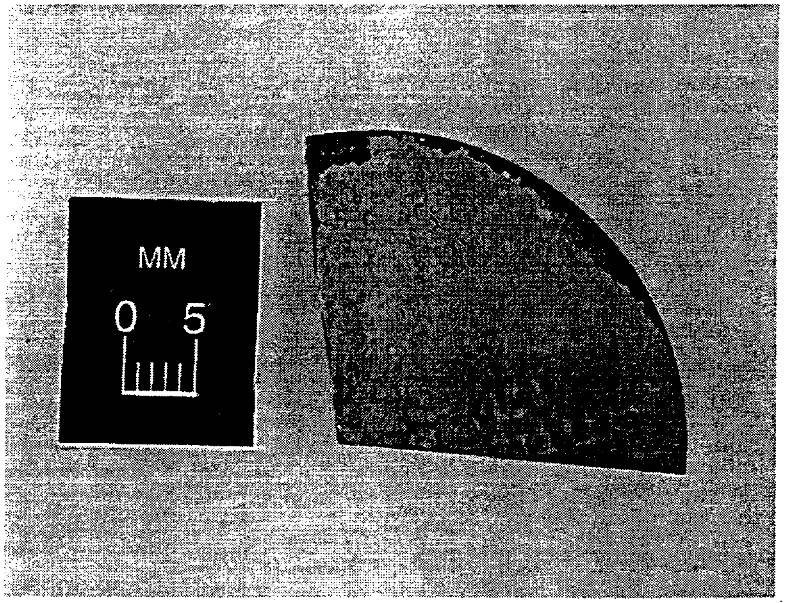

Figure 3: Nicalon fiber-reinforced SiC matrix composite coated with sintered CMZP (doctor-blade process)

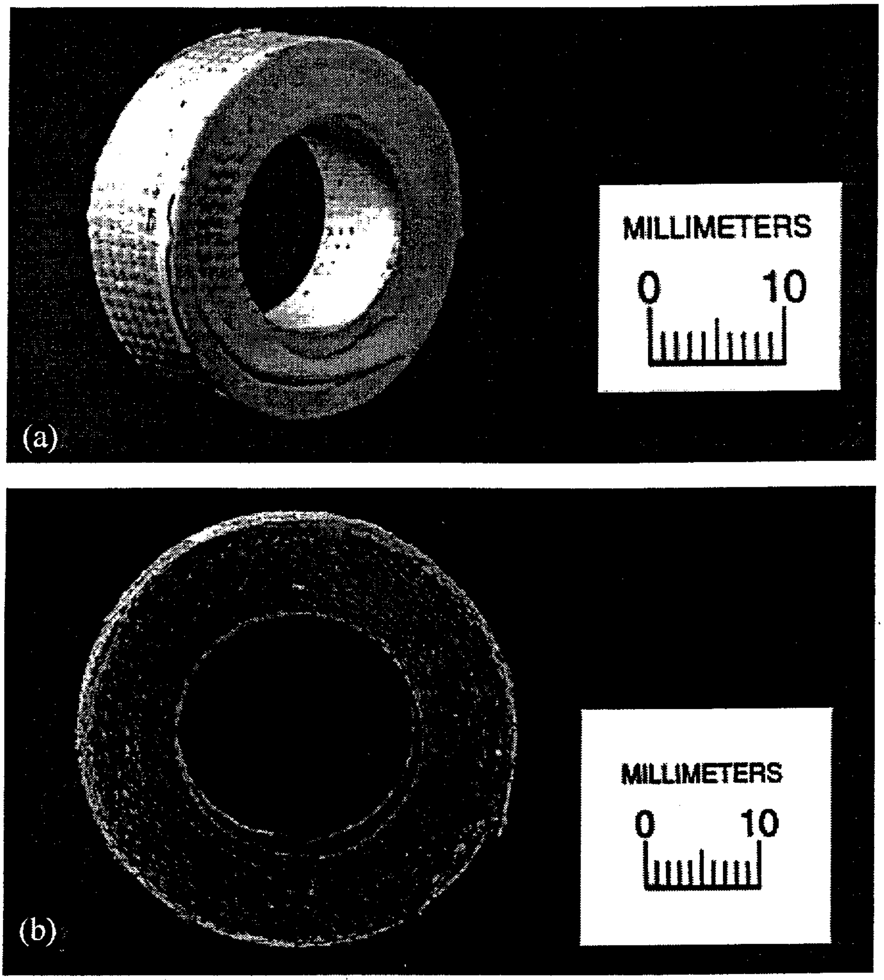

Figure 4: Examples of (a) thick and (b) thin CS50 coatings (dip-coating process)

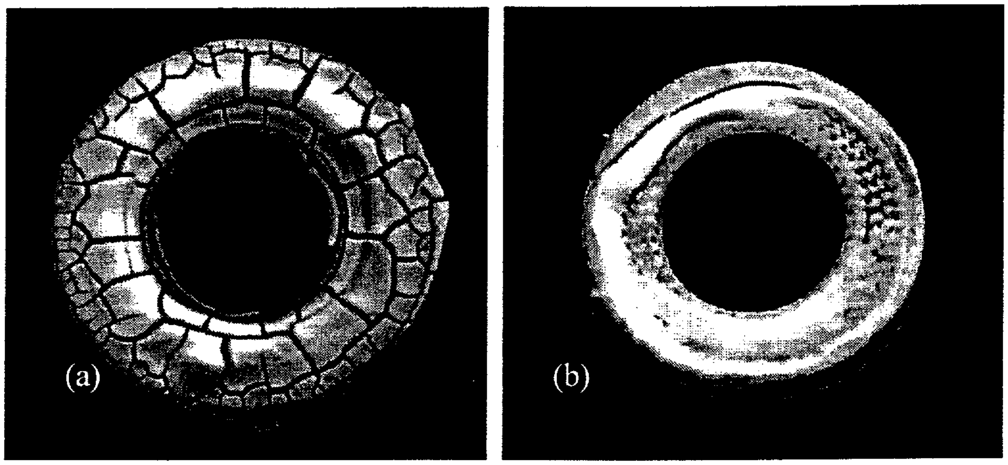

Figure 5: Influence of ZnO on coating quality, (a) without ZnO, (b) with ZnO

Analysis

X-ray Diffraction

The diffraction patterns indicated that CMZP and CS-50 were present. No other phases were detected.

Microscopy

Pictures of different CS50 and CMZP coatings obtained by optical microscopy are seen in Fig. 6. The coatings are very uniform, and no gap or debonding can be seen at the coating matrix interface. The CMZP coating, obtained by the tape casting method, is much thinner than the CS-50 coating obtained by dip-coating.

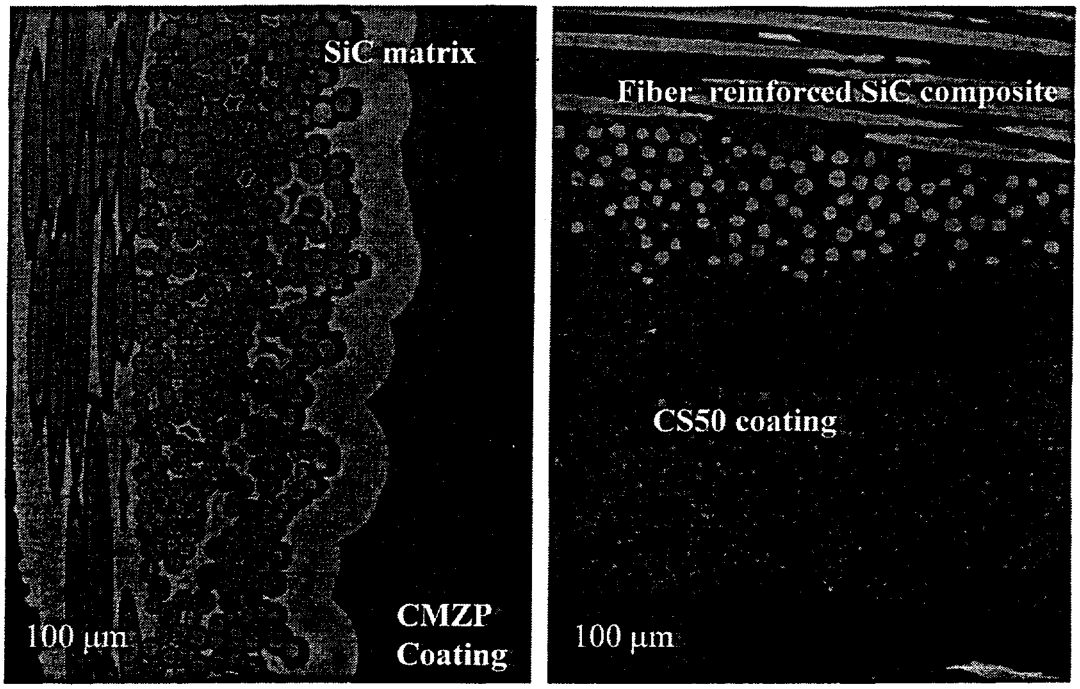

Figure 6: Optical micrographs of CS-50 and CMZP coatings

Corrosion Resistance of the Coatings

No major weight loss was observed for both coated and reference samples after exposure. The samples used in the study were very porous, consequently, the sodium sulfate flowed into the pores and lowered the surface loading to less than 8 mg/cm^2. No sign of degradation was found on the coated samples, but a white deposit was visible on both non-coated composites. No sign of microstructure degradation was observed during microscopic evaluation of the polished samples. Samples were then broken and observed with a SEM. Fig. 7 and 8 are SEM micrographs of non-coated Nextel fiber-reinforced SiC matrix composites before and after corrosion. The corroded, non-coated samples contain a very glassy phase indicating degradation of the SiC matrix. In contrast, coated (CS50) samples show very little degradation as illustrated in Fig. 9 and 10 which are different samples (A,B). EDX results indicate that sodium was present in the CS50 coating, but not in the composite. Thus, most of the sodium was trapped in the coating, which prevented the degradation of the substrate.

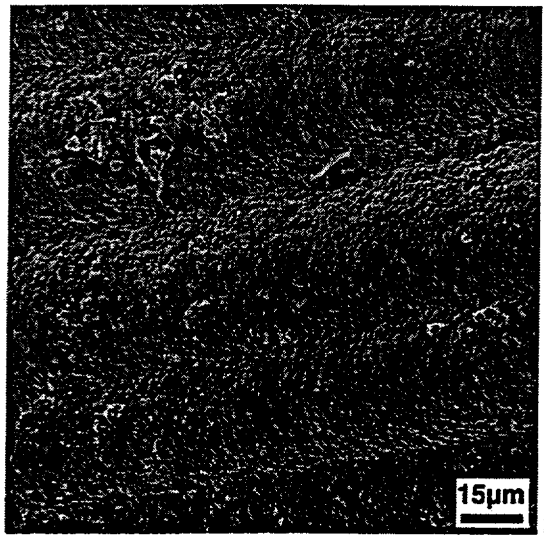

Figure 7: Non-corroded, non-coated composite

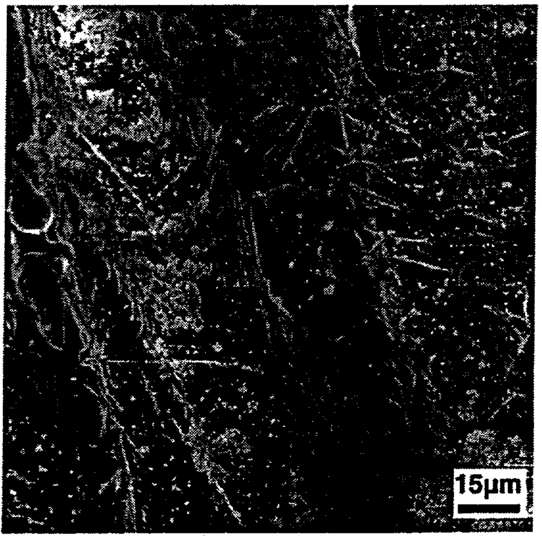

Figure 8: Corroded, non-coated composite

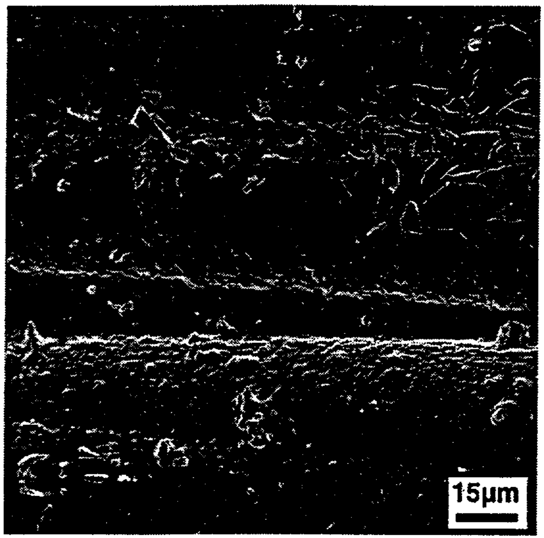

Figure 9: Corroded, coated with CS-50, A

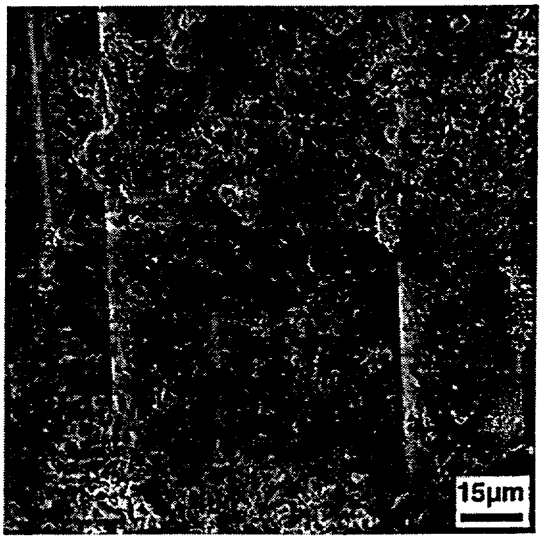

Figure 10: Corroded, coated with CS-50, B

CONCLUSIONS

A good quality, relatively inexpensive coating process for applying protective oxide coatings on SiC matrix materials has been developed, and an understanding of the most critical factors controlling the process has been obtained. The glaze-like behavior of both NZP materials obtained with ZnO additions was beneficial to the quality of the coating. The corrosion resistance behavior of the coatings is very encouraging, and further improvements in coating quality should make NZP coatings even more efficient in terms of corrosion protection.

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