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High-Temperature Corrosion of Nicalon®/SiC Composites

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*Fossil
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HIGH-TEMPERATURE CORROSION OF NICALON[®]/SiC COMPOSITES*

R. A. Lowden and R. D. James[†]

ABSTRACT

The elevated-temperature stability of Nicalon[®] (Nippon Carbon Company, Tokyo, Japan)/SiC composites with a graphitic carbon interface layer in oxidizing and simulated fossil fuel environments was investigated. Composite specimens with and without an external SiC surface coating were oxidized in air and exposed to a variety of combustion environments at a temperature of 1273 K. A burner rig furnace was constructed for simulating corrosive fossil fuel environments containing water vapor, sulfur, and sodium. The mechanical properties of unprotected Nicalon[®]/SiC specimens were degraded after short periods of exposure, due to the oxidation of the carbon interface coating. Longer exposures resulted in the oxidation of the fibers and matrix to form silica, which with time bonded the components together and produced brittle behavior. Combustion environments hastened the embrittlement of composites without an external SiC coating. Conversely, the specimens protected by a chemical vapor deposition (CVD) SiC surface coating exhibited only small decreases in strength after oxidation or corrosion in combustion environments. The SiC layer sealed off the surface of the composites, protecting the exposed fibers' ends, and thus prevented oxidation at the fiber-matrix interface.

1. INTRODUCTION

The efficiency of many energy conversion and industrial processes can be improved by simply increasing operating temperatures and pressures. Such environments, however, require materials with exceptional high-temperature mechanical properties and corrosion resistance. Ceramics exhibit excellent high-temperature strength and

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stability, and thus are leading candidates for use in the critical components of high-temperature combustion and power generation systems. However, the utilization of conventional ceramics in these high-temperature, high-stress applications is hindered by their inherent brittleness and lack of damage tolerance.

One method of improving the fracture properties of a ceramic is the addition of fibers. The incorporation of high-strength fibers to brittle glass and ceramic matrices has produced substantial increases in strength, crack resistance, and work of fracture in many of these materials.¹⁻³ Fiber-reinforced ceramic composites are currently being evaluated for an assortment of high-temperature applications.^{4,5} The commercial availability of a variety of continuous ceramic fibers, coupled with recent advances in the processing of ceramic matrices, has resulted in significant activity in the development, characterization, and utilization of continuous fiber-reinforced ceramic composites.

To date, emphasis in the development of these advanced materials has been placed on processing and mechanical properties. Glass-ceramic and ceramic matrices are being reinforced with polymer-derived Si-C-O fibers, and moderate quantities of these materials are being fabricated using a variety of techniques.¹⁻⁶ Although exceptional room- and elevated-temperature properties have been reported, only limited information has been presented regarding the stability of these composite systems in simulated service environments. High-temperature corrosion can have detrimental effects on the fibers and matrices and thus affect the properties of the composites. These issues must be addressed before final acceptance of these materials for critical components in elevated-temperature commercial applications.

It is well known that, although the fibers and matrix play major roles in determining the final properties of a composite, the fiber-matrix interface has a significant influence on the fracture behavior and mechanical properties of reinforced ceramics.⁷⁻⁹ Typically, coatings are used to protect ceramic fibers from chemical attack during processing and to control interfacial forces.^{8,9} Carbon, whether intentionally deposited on the fibers prior to consolidation^{8,9} or formed serendipitously during processing,¹⁰ is the most commonly used interlayer in ceramic composites

today. Carbon coatings have performed well in a variety of systems; however, the poor oxidation resistance of carbonaceous materials has prompted intense scrutiny of their usefulness at elevated temperatures in oxidizing environments. Thus, the present investigation examined the effects of elevated-temperature exposure to corrosive environments on the interface and properties of Nicalon[®]/SiC composites with a graphitic carbon interface layer.

2. EXPERIMENTAL PROCEDURE

2.1 COMPOSITE FABRICATION

Fibrous preforms were fabricated by stacking multiple layers of Nicalon plain-weave fabric rotated in a $0 \pm 30^\circ$ sequence within the cavity of a graphite holder. The layers were hand compressed to produce a preform with a nominal loading of 40 vol. % fiber and were held in place by a perforated graphite lid pinned to the holder. The cloth sizing was removed through multiple washings with acetone. The nominal size of the disk-shaped fibrous preforms was 75 mm in diameter and 16-mm thick.

Preforms were next precoated with an $\approx 0.3\text{-}\mu\text{m}$ layer of carbon, deposited from an argon/propylene mixture at 1375 K and 3.3 kPa pressure. The thickness of the interface coating was determined from weight gain and post-infiltration polarized light microscopic examination of polished composite cross sections. The preforms were densified with SiC using a forced-flow, thermal-gradient chemical vapor infiltration (FCVI) technique, which has been previously described in detail.^{6,8,9,11} The SiC matrix was produced by the decomposition of methyltrichlorosilane (CH_3SiCl_3 or MTS) in hydrogen using a hot-surface temperature of 1473 K and atmospheric pressure. Processing times were ≈ 40 h and the infiltrated composite samples had a nominal density of 2.6 g/cm^3 , approximately 85 to 90% of theoretical density.

Bars were cut from the samples parallel to the 0° orientation of the top layer of cloth using a diamond saw, and tensile and compression surfaces were ground parallel to the long axis of the specimen. The average dimensions of the test bars from the composite samples were $3 \times 4 \times 50$ mm and all specimens were measured and weighed to determine

densities. A portion of the flexure specimens were coated with a 40- μm SiC layer deposited from MTS in hydrogen at 1473 K and 3.3 kPa. The thickness of the SiC external coating was determined from weight gain and geometrical surface area measurements.

2.2 OXIDATION/CORROSION

Composite specimens were oxidized in static air at 1273 K for 100, 500, and 1000 h. Flexure bars with and without SiC surface coatings were placed in the cavity of an atmospheric box furnace and heated to temperature at a rate of 300°/h. Once the furnace achieved equilibrium, the final temperature was measured using a hand-held optical pyrometer and then maintained using a thermocouple-controlled programmer. At the specified time, the furnace was shut off and allowed to cool unassisted.

A burner rig furnace, shown in Fig. 1, was employed to examine the corrosion of the Nicalon[®]/SiC composite specimens in simulated combustion environments.^{12,13} Constant temperature was maintained by a resistively heated clam shell furnace, and an alumina tube was used as a combustion chamber. Concentric alumina tubes carried natural gas, air, and other

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Fig. 1. Schematic of the burner rig furnace.

gases into the hot zone where they mixed and burned. A platinum wire mesh affixed to the outlet of the burner tube ensured ignition of the gases. Mass flow controllers were used to regulate gas flows, with total flow maintained at a nominal 5.5 l/min in all experiments.

Flexure bars were arranged laterally on an aluminum oxide base placed approximately 25 cm from the burner outlet. The furnace was heated to 1273 K and allowed to equilibrate. Combustion gases were then introduced to the system and conditions were held constant for 100 h, upon which the reactant flows were terminated and the furnace allowed to cool. Building-supplied air and natural gas were used with a fuel-to-air ratio of 0:1. The equilibrium compositions of the burner rig atmospheres, calculated using SOLGASMIX-PV,¹⁴ are given in Table 1.

Table 1. Calculated composition of combustion atmospheres

Species	Combustion product gases		
	Gas/air	+ 1% H ₂ S (vol %)	+ Na ₂ CO ₃
N ₂	71.2	70.9	71.2
H ₂ O	15.7	14.7	15.7
CO ₂	9.3	9.3	9.3
O ₂	1.9	1.4	1.9
NO _x	1.8	2.5	1.8
H ₂ SO ₃	--	1.0	--
Na ₂ O	--	--	≈ 80 ppm Na

Sulfur-containing atmospheres, which can result from the burning of fossil fuels such as coal, were simulated by adding hydrogen sulfide gas, H₂S, to the combustion gas mixture. A sulfur content of 1% was selected from consideration of various sources¹⁵⁻¹⁷ and was obtained by adding 50 cm³/min H₂S to the gas/air mixture. It was expected that the addition of sulfur would result in the production of H₂SO₃ in the combustion gas. The effects of the addition of the sulfur-containing gas on the combustion products of natural gas and air are also displayed in Table 1.

Sodium carbonate was used as the source of sodium in the experiments.¹⁷⁻¹⁹ An aluminum oxide boat was filled with Na₂CO₃ and

sintered at 1173 K for 24 h. The sintered sample was placed in the burner rig furnace upstream from the composite specimens and heated to 1173 K. Sodium carbonate vapor was carried to the samples by passing a portion of the combustion air over the boat. A Na_2CO_3 flow of $\approx 0.25 \text{ cm}^3/\text{min}$ was calculated from the weight change of the sintered sample, producing $\approx 80 \text{ ppm Na}$ in the gas mixture.

2.3 CHARACTERIZATION

Room-temperature flexure strengths for as-fabricated and the treated composites were measured in four-point bending. A support span of 40 mm, a loading span of 20 mm, and a crosshead speed of 0.508 mm/min were used, and all specimens were loaded perpendicular to the layers of cloth. Load-displacement curves were recorded to examine the fracture process and determine the loads for ultimate strength calculations. Six coated and uncoated specimens were tested for each exposure.

The fracture surfaces of the specimens were examined using a scanning electron microscope (SEM). Specimens that did not completely part during flexure testing were broken by hand so that the fracture surfaces could be examined. Polished specimen cross sections were prepared using standard metallographic techniques and were examined using optical microscopy. Detailed characterization of the effects of environmental exposure on the interfacial regions of the composites was also performed employing electron microprobe and transmission electron microscopy (TEM) techniques.

3. RESULTS

3.1 OXIDATION IN AIR

Although the exposures to 1273 K in air produced a slight discoloration of the SiC-coated specimens (suggesting some degree of oxidation), the strengths of the specimens were unaffected. Flexure strengths in excess of 300 MPa were maintained even after 1000 h (Fig. 2). In contrast, all unprotected specimens exhibited a significant loss in flexure strength even after only 100-h exposures. The detrimental effects of oxidation on the fracture behavior (i.e., fiber pullout and toughness)

Fig. 2. The effect of oxidation in air at 1273 K on the flexure strength of Nicalon[®]/SiC composites with a carbon interlayer.

of the unprotected specimens were found to be progressive. The change in behavior was most apparent in the flexure behavior and the condition of the fracture surfaces of the specimens (Figs. 3 and 4). A loss of strength was observed for the composite specimens without a SiC external coating after 100 h in air at 1273 K. However, the composites continued to exhibit gradual failure accompanied by extensive fiber pullout (Fig. 4). As exposure time was increased, the degree of fiber pullout diminished, eventually resulting in completely brittle fracture (Fig. 3).

Electron microprobe analysis of oxidized composite specimens with and without a SiC surface coating revealed a loss of the carbon interface

Fig. 3. The progressive effects of oxidation on the flexure behavior of unprotected specimens, time in h indicated on curves.

Fig. 4. The effects of exposure time on the fracture surfaces of Nicalon[®]/SiC composites: (a) as-fabricated, (b) 100 h, (c) 500 h, and (d) 1000 h.

coating in the unprotected samples even after only 100-h oxidation (Fig. 5). The lack of carbon in the oxidized specimen is noted by the diminished carbon K_{α} X-ray signal intensity at the fiber-matrix interface. TEM accompanied by energy-dispersive X-ray analysis (EDX) of the composites embrittled by longer exposure times showed that an amorphous silica layer had replaced the carbon coating at the fiber-matrix interface throughout the specimens (Fig. 6).

YP12164

Fig. 5. Back scatter electron images and carbon K_{α} elemental dot maps of composite specimens: (a) with and (b) without a SiC coating after 100-h oxidation in air at 1273 K.

3.2 CORROSION IN COMBUSTION ENVIRONMENTS

Exposure of SiC-coated and unprotected composite specimens to the combustion products of natural gas and air at 1273 K resulted in strengths similar to those produced by oxidation in air (Fig. 7). However, the embrittlement of unprotected composites was much more rapid. After only 100-h exposure to the combustion environments, the composites without a SiC outer layer exhibited low strength and catastrophic, brittle fracture.

Fig. 6. TEM micrographs of the interface region for composites: (a) with and (b) without a SiC external layer after 1000-h oxidation in air at 1273 K.

Fig. 7. Comparison of composite flexure strengths after 100 h, 1273 K exposures to various corrosion environments.

TEM analysis again showed the carbon interlayer was removed and oxidation of the fibers and matrix resulted in the formation of an amorphous silica layer at the interface after 100 h. This was a highly accelerated rate compared to the composites heated in air.

The hypothesis of an accelerated oxidation rate at the fiber-matrix interface was supported by comparison of oxygen K_{α} X-ray maps of unexposed specimens and specimens after 100 h in air and in gas/air combustion gases. The fibers, composed of Si, C, and O, are easily identified in the as-fabricated samples [Fig. 8(a)]. There appears to be slight oxidation of the fiber surfaces in the composite heated in air, as noted by the thinner oxygen-rich band (lighter areas of the dot maps) that is limited to the fiber surfaces [Fig. 8(b)]. The intensity of the oxygen-rich zones at the fiber surface is accentuated by the darker areas surrounding them. This is most likely due to the fact that there would be a gap between the fibers and matrix at this stage of oxidation. The carbon interlayer has been removed and the exposed matrix and fiber surfaces have just begun to oxidize. Higher oxygen concentrations at the fiber-matrix interface were found in the composites exposed to the combustion environment [Fig. 8(c)]. The increased level of oxidation is shown by the elevated intensity of the O K_{α} X-ray signal and the width of the oxygen-rich zone at the fiber-matrix interface in the unprotected samples after exposure to the gas/air combustion products.

The presence of sulfur seemed to exacerbate the degradation of the strength for all specimens, with and without a SiC external coating. As for uncoated composites exposed to the combustion of natural gas in air without sulfur, unprotected bars possessed low strength and no evidence of fiber pullout. The strengths of the SiC-coated samples were slightly lower than all protected samples, regardless of exposure time and/or atmosphere (Fig. 7). Microprobe analysis found no evidence of sulfur in the SiC-coated specimens. Sulfur could only be found in secluded pockets along the fiber-matrix interface in the unprotected samples (Fig. 9).

A thick reaction layer was formed on the surfaces of all specimens tested in a sodium-containing environment. The surface layer was the result of the corrosion of the protective SiC coating and, for the unprotected samples, of the matrix and fibers (Fig. 10). Unprotected

YP12165

(a)

(b)

(c)

Fig. 8. K_{α} O dot maps for uncoated composite specimens: (a) unexposed, (b) 100 h at 1273 K in air, and (c) 100 h at 1273 K in gas/air combustion products.

Fig. 9. An oxygen elemental map and sulfur line scan for an unprotected composite after 100-h exposure at 1273 K to the combustion of natural gas in air with 1% H_2S .

Fig. 10. Micrograph of glass layer formed during exposure to Na-containing combustion atmosphere: (a) SiC protective coating and (b) unprotected.

specimens were weak and brittle. The carbon interlayer remained intact in SiC-coated samples and flexure strengths were only slightly decreased. Flexure strength data for the Na corrosion specimens are also presented in Fig. 7. Microprobe analysis of the specimens without a SiC external coating found sodium at the fiber-matrix interface throughout the composite (Fig. 11).

YP12166

Fig. 11. Oxygen and sodium elemental maps for an unprotected composite after 100-h exposure at 1273 K to the combustion of natural gas in air with ≈ 80 ppm Na.

4. DISCUSSION

The poor oxidation resistance of carbon is well known.²⁰ Carbon begins to oxidize at temperatures around 700 K and oxidation is rapid in air at temperatures above 1173 K. Oxidation rates of $\approx 10^{-3}$ g/cm²-min, or about 5 μ m/min, at 1273 K in air are typical for pyrolytic graphite.²⁰ The oxidation of Nicalon[®]/SiC composites begins by attack of the carbon interface coating at exposed fiber ends. With the fibers

lying in one plane, oxidation proceeds along the fiber lengths. As the carbon interlayer oxidizes, carbon is in equilibrium with carbon monoxide, and thus a unitary carbon activity is maintained along the fiber-matrix interface. Oxidation of the fibers and matrix is therefore hindered. Once the carbon is removed along the entire fiber length, the matrix and fiber oxidize to form a silica layer that eventually bonds the components together. The strong bond at the fiber-matrix interface does not permit debonding and sliding, resulting in brittle behavior. Also, oxidation degrades the properties of the fiber, enhancing the embrittlement of the composite.

This type of "pipeline" oxidation has been observed in other similar composite systems.^{5,21,22} In contrast, the carbon interlayer remained unaltered in specimens with a SiC surface coating even after 1000 h. The ends of the fibers and the fiber-matrix interface layer were not exposed, thus hindering oxidation of the carbon interlayer and composite constituents.

A distinct boundary could be detected in the amorphous silica layer that was formed at the fiber-matrix interface. It is speculated that this interface, which appeared to be positioned similarly in all highly corroded specimens, was present due to the difference in the oxidation rates of the fibers and matrix. The oxidation rate of CVD SiC is extremely slow at temperatures below 1473 K.^{17,23,24} Only a very thin oxidation layer (noted as a slight discoloration of the surfaces) was observed for all heat-treated composites with the exception of those exposed to a sodium-containing atmosphere. It is reported, however, that the Nicalon fibers, because they are composed of SiC, SiO₂, and C,^{25,26} oxidize more rapidly than CVD SiC, thus producing a thicker SiO₂ layer than at the matrix surface.

The oxidation rates of both SiC and C are accelerated by the presence of water vapor, sulfur, and sodium.^{16,17} The unprotected samples, exposed to the combustion products of natural gas and air at 1273 K (which contain approximately 15 vol % water vapor), exhibited brittle failure after only 100 h. Compositional analysis of these composites found high concentrations of oxygen at the fiber-matrix

interface, confirming the proposed increased rate of oxidation of the fibers and matrix. The presence of sulfur produced an additional decrease in strength in all exposed specimens. Microprobe analysis found sulfur in small segregated pockets along the fiber-matrix interface. There was no even distribution of the sulfur throughout the composite structures and components and, thus, the mechanisms of degradation are unclear.

Sodium additions to the test environment produced very thick reaction layers on the surface of the specimens. Alkali oxides such as Na_2O react with silicon-based materials to form low melting point phases.¹⁹ When the normally protective silica surface film is contaminated with Na_2O , a lower melting temperature glass with higher oxygen diffusivity results. This allows oxidation to proceed more quickly at the SiO_2/SiC interface, causing rapid recession and consumption of the SiC. This effect was most evident for the unprotected specimens where oxidation of the carbon interlayer and composite constituents proceeded quickly in the Na-containing atmosphere. Extensive consumption of the fibers and matrix near the external surfaces was observed. The SiC external seal coating appeared to provide adequate protection for the interface, fibers, and matrix in these limited exposures. However, it is clear that continued exposure would result in gross corrosion of the protective SiC surface coating and, finally, of the composite, resulting in a significant degradation of performance.

5. CONCLUSIONS

Investigation of the effects of oxidation and corrosion of Nicalon[®]/SiC composites with a carbon interlayer confirmed the need for a protective external coating. The mechanical properties of uncoated composite samples were degraded after short periods of oxidation in air. It appears this is due to the complete oxidation of the carbon interlayer throughout the composite specimens. Longer exposure produced brittle behavior as the fibers and matrix oxidized to form a silica interlayer, bonding the components together too strongly. A CVD SiC

coating, however, protected the composites against oxidation by sealing off the exposed fibers on the surface of the sample.

Combustion environments hastened the embrittlement of unprotected samples. Water vapor and sulfur accelerated the oxidation process. Exposure to sodium weakened the composites by reacting with the ceramic components to form a thick surface film, most likely a soda-glass corrosion product. The rapid consumption of the composites in the Na-containing atmosphere indicated that, although the SiC seal coating is helpful in oxidizing atmospheres, it may not be resistant to long-term attack by sodium at elevated temperatures.

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