MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0310598 5

ornl

ORNL/TM-11893

OAK RIDGE
NATIONAL
LABORATORY

MARTIN MARIETTA

High-Temperature Corrosion of Nicalon®/SiC Composites

R. A. Lowden
R. D. James

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500N ROOM 175
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this report, send in name with report and the library will arrange a loan.

Fossil
Energy
Program

MANAGED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-11893

Metals and Ceramics Division

HIGH-TEMPERATURE CORROSION OF NICALON®/SiC COMPOSITES

R. A. Lowden and R. D. James

Date Published: August 1991

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

Prepared for the
U.S. Department of Energy
Office of Fossil Energy
Advanced Research and Technology Development Materials Program
AA 15 10 10 0

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
managed by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

MARTIN MARIETTA ENERGY SYSTEMS LIBRARIES

3 4456 0310598 5

TABLE OF CONTENTS

	Page
LIST OF FIGURES	v
ABSTRACT	1
1. INTRODUCTION	1
2. EXPERIMENTAL PROCEDURE	3
2.1 COMPOSITE FABRICATION	3
2.2 OXIDATION/CORROSION	4
2.3 CHARACTERIZATION	6
3. RESULTS	6
3.1 OXIDATION IN AIR	6
3.2 CORROSION IN COMBUSTION ENVIRONMENTS	10
4. DISCUSSION	15
5. CONCLUSIONS	17
6. ACKNOWLEDGMENTS	18
7. REFERENCES	18

LIST OF FIGURES

Figure		Page
1	Schematic of the burner rig furnace	4
2	The effect of oxidation in air at 1273 K on the flexure strength of Nicalon®/SiC composites with a carbon interlayer	7
3	The progressive effects of oxidation on the flexure behavior of unprotected specimens, time in h indicated on curves	8
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	9
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	10
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	11
7	Comparison of composite flexure strengths after 100 h, 1273 K exposures to various corrosion environments	11
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	13
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	14
10	Micrograph of glass layer formed during exposure to Na-containing combustion atmosphere: (*a*) SiC protective coating and (*b*) unprotected	14
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	15

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 environements. 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

*Research sponsored by the U.S. Department of Energy, Office of Fossil Energy, Advanced Research and Technology Development Materials Program [DOE/FE AA 15 10 10 0, Work Breakdown Structure Element ORNL-1(C)] under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

†Clemson University, Clemson, South Carolina.

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 ± 30° 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 ≈ 0.3-μm 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 × 4 × 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

ORNL DWG 91-9691

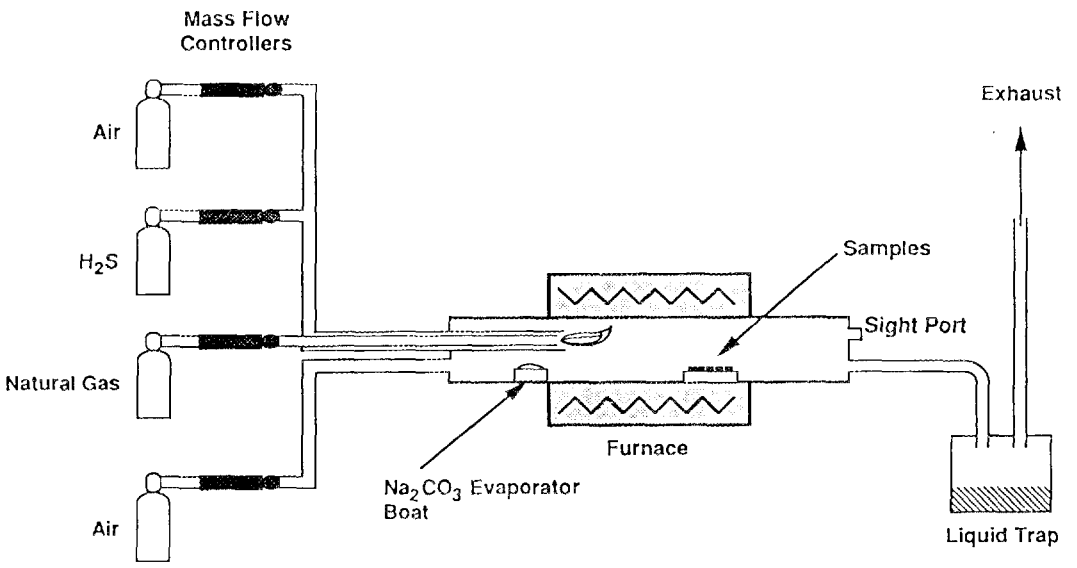


Fig. 1. Schematic of the burner rig furnace.

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

	Combustion product gases		
Species	Gas/air	+ 1% H_2S (vol %)	+ Na_2CO_3
N_2	71.2	70.9	71.2
H_2O	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_2SO_3	--	1.0	--
Na_2O	--	--	≈ 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, H_2S, to the combustion gas mixture. A sulfur content of 1% was selected from consideration of various sources[15-17] and was obtained by adding 50 cm^3/min H_2S to the gas/air mixture. It was expected that the addition of sulfur would result in the production of H_2SO_3 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 Na_2CO_3 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 ≈ 0.25 cm^3/min was calculated from the weight change of the sintered sample, producing ≈ 80 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)

ORNL DWG 90-9705

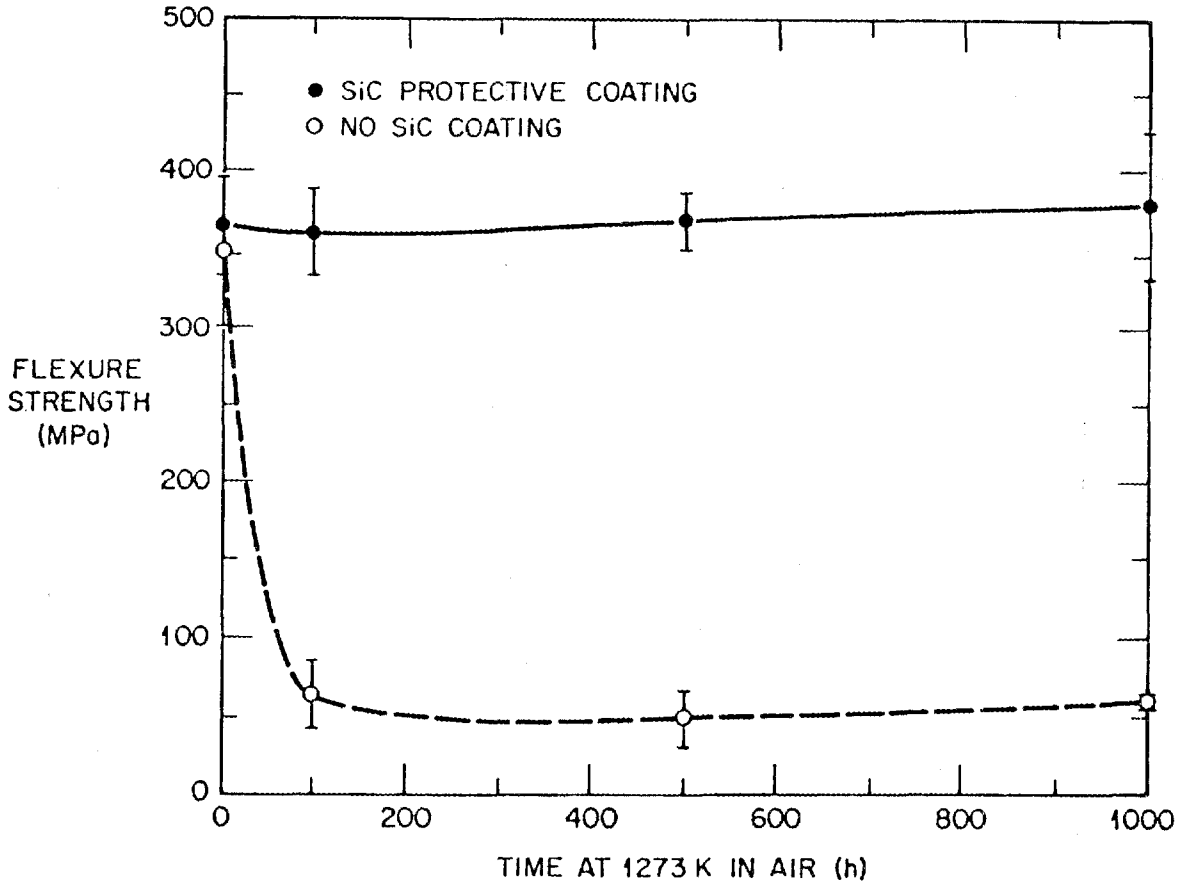


Fig. 2. The effect of oxidation in air at 1273 K on the flexure strength of Nicalon®/SiC composites with a carbon interlayer.

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

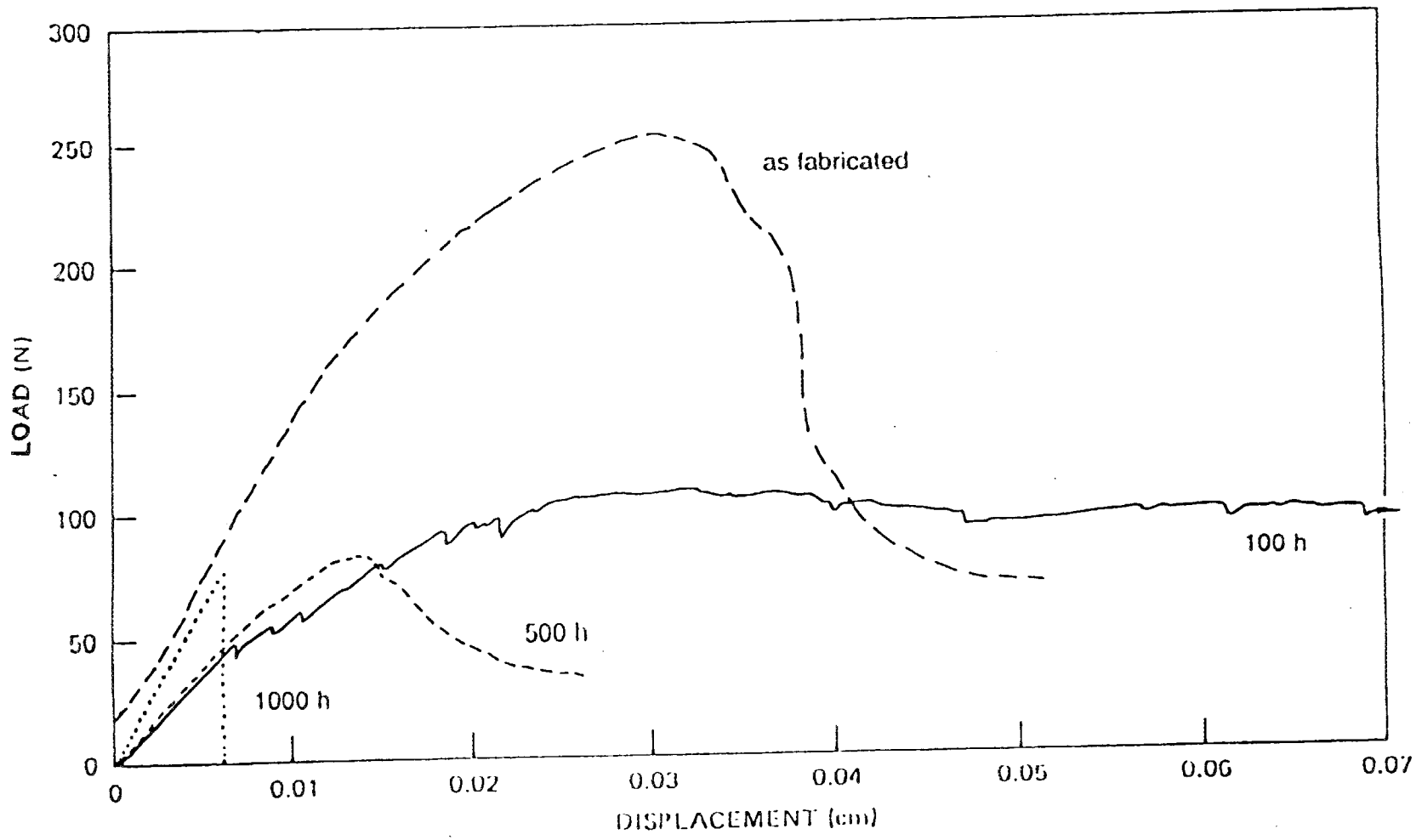


Fig. 3. The progressive effects of oxidation on the flexure behavior of unprotected specimens, time in h indicated on curves.

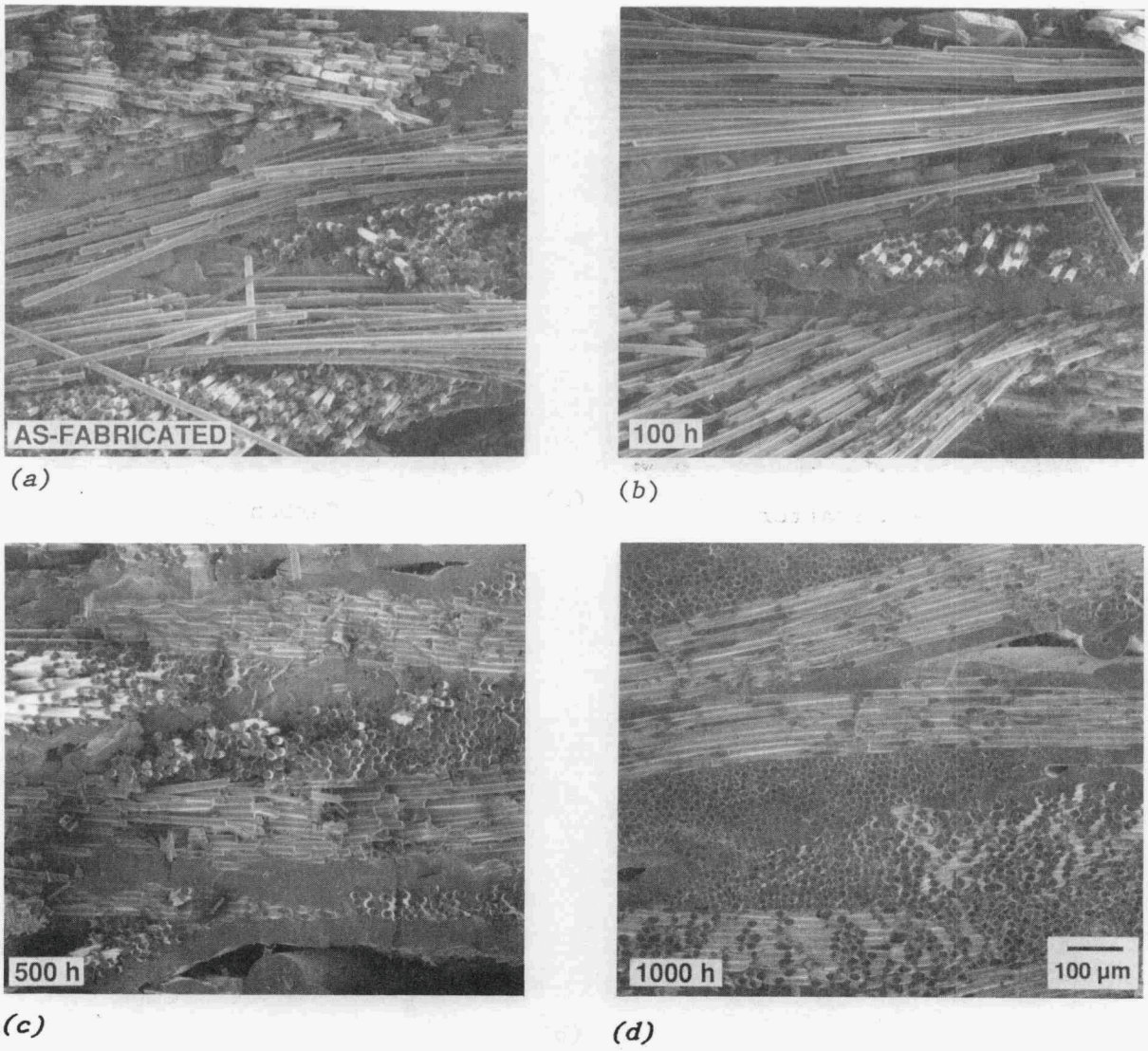


Fig. 4. The effects of exposure time on the fracture surfaces of Nicalon®/SiC composites: (*a*) as-fabricated, (*b*) 100 h, (*c*) 500 h, and (*d*) 1000 h.

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

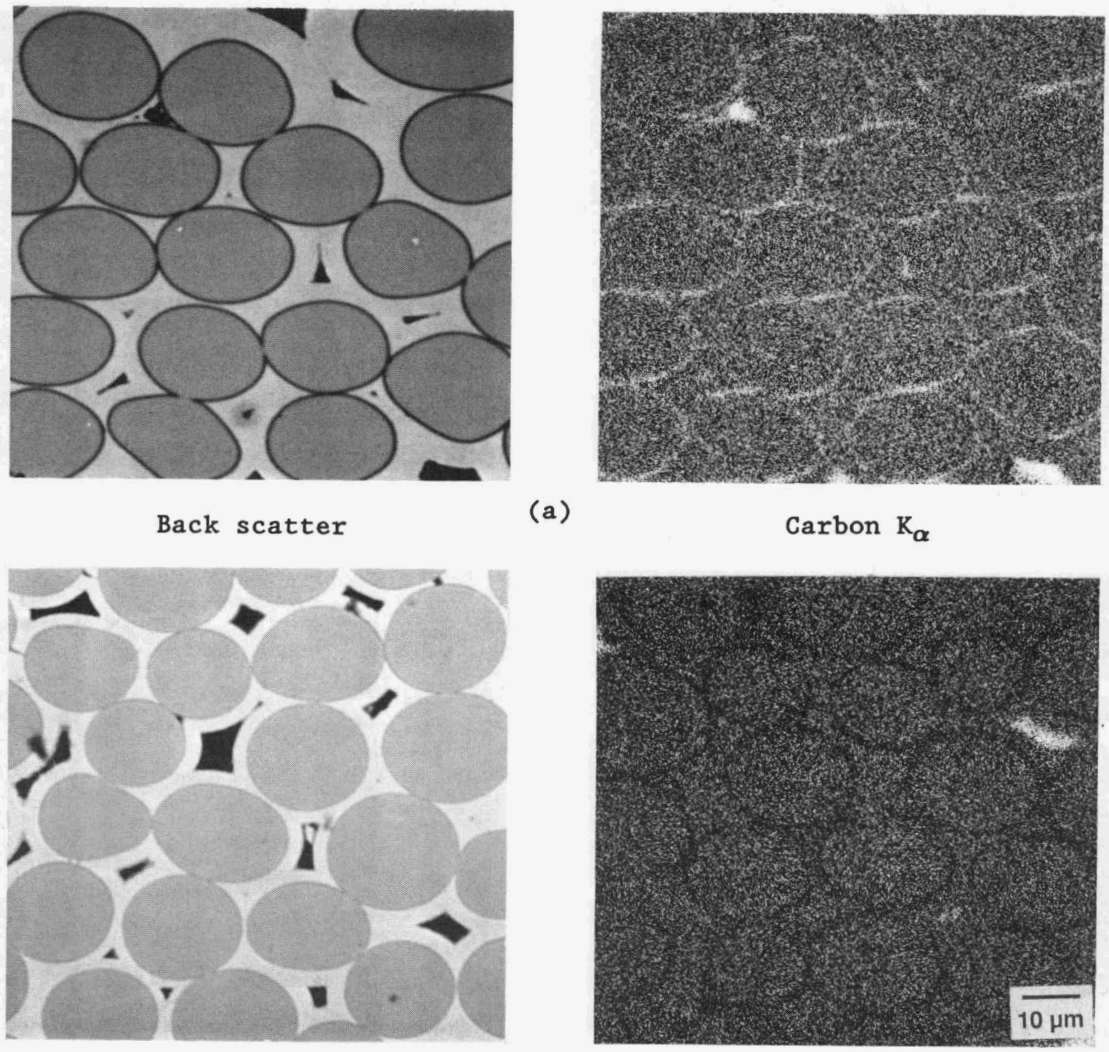
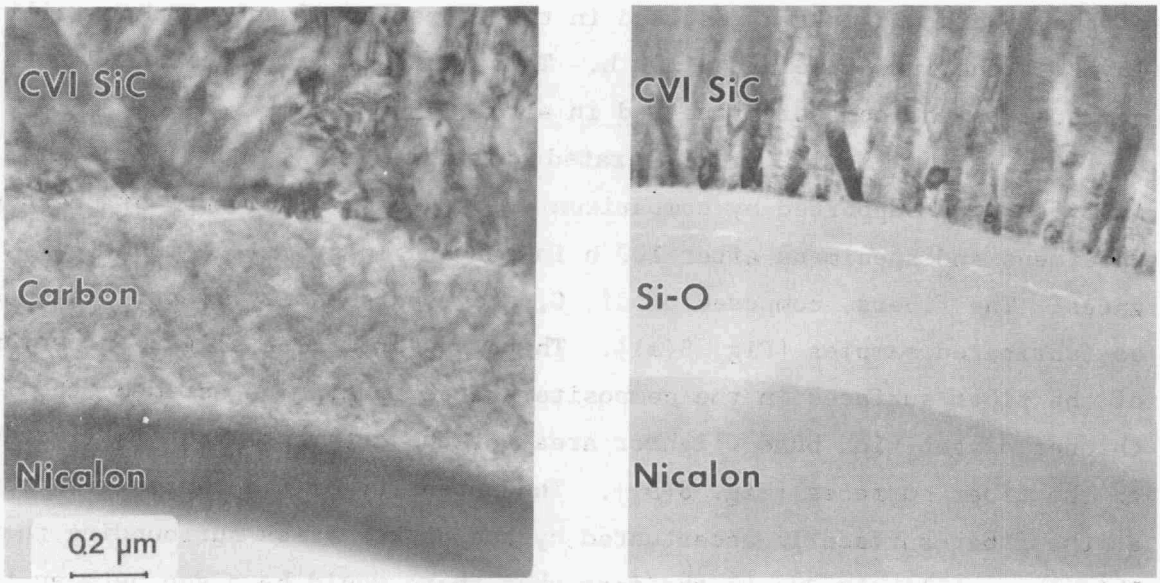


Fig. 5. Back scatter electron images and carbon K_α elemental dot maps of composite specimens: (*a*) with and (*b*) without a SiC coating after 100-h oxidation in air at 1273 K.

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.

YP10736



(*a*) (*b*)

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.

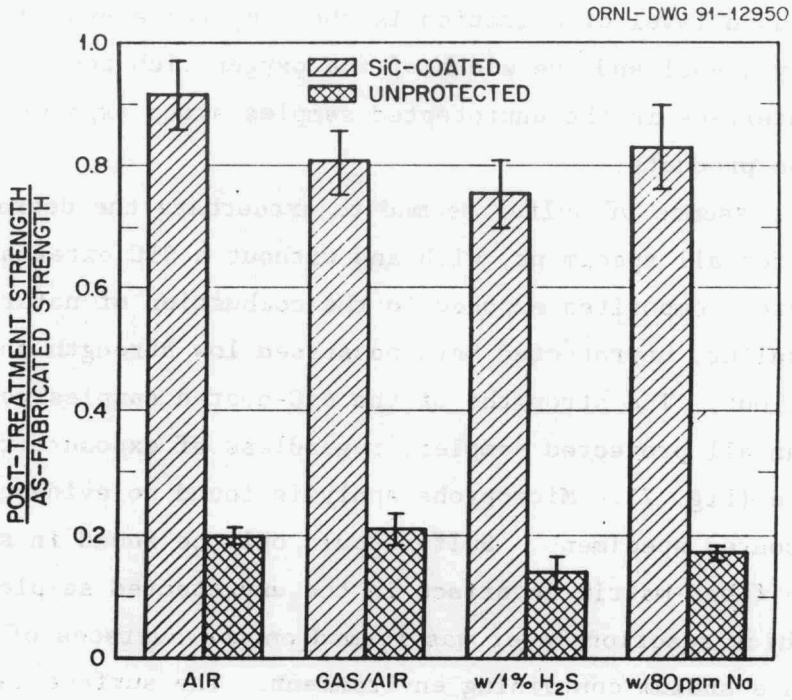


Fig. 7. Comparison of composite flexure strengths after 100 h, 1273 K exposures to various corrosion environments.

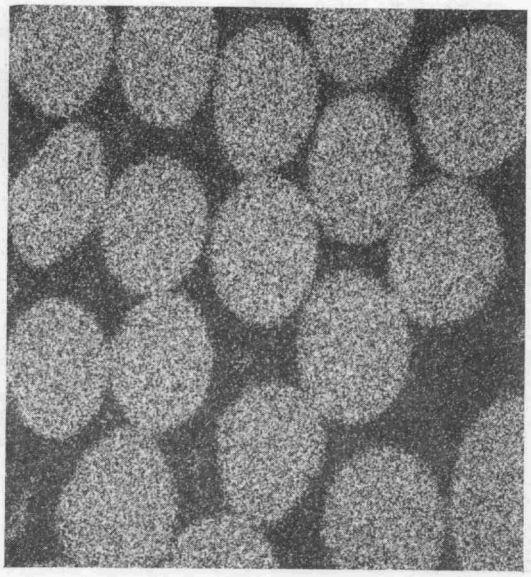
TEM analysis again showed the carbon interlayer was removed and oxidation of the fibers and matrix resulted in the formation of an amorphous silica layer at the interface after 100 h. This was a highly accelerated rate compared to the composites heated in air.

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.

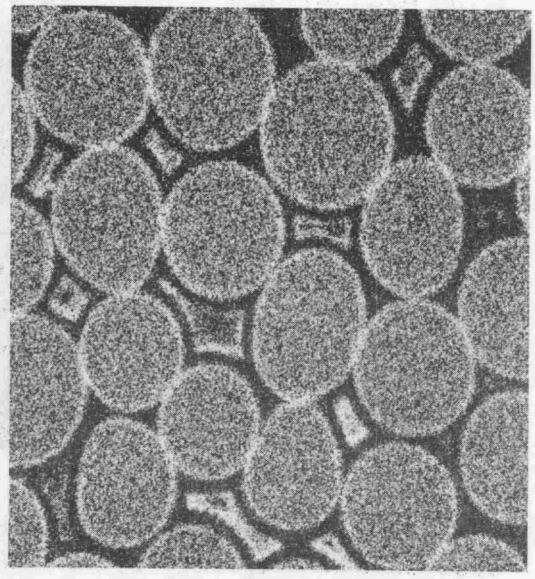
The presence of sulfur seemed to exacerbate the degradation of the strength for all specimens, with and without a SiC external coating. As for uncoated composites exposed to the combustion of natural gas in air without sulfur, unprotected bars possessed low strength and no evidence of fiber pullout. 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

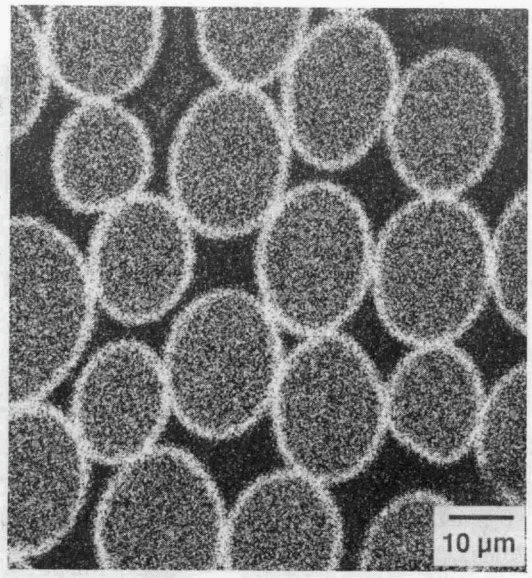
YP12165



(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.

YP12167

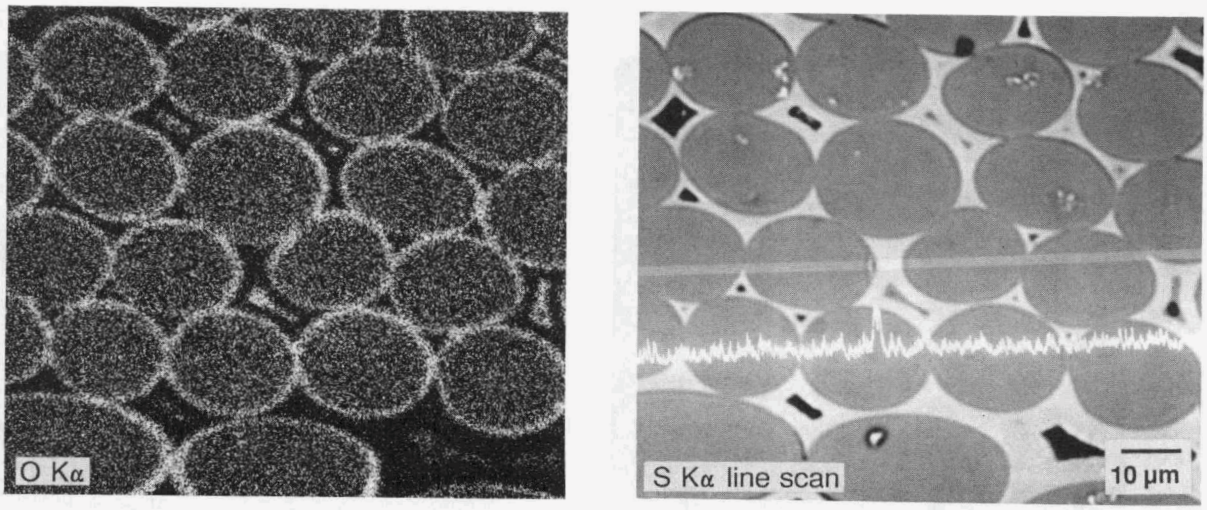
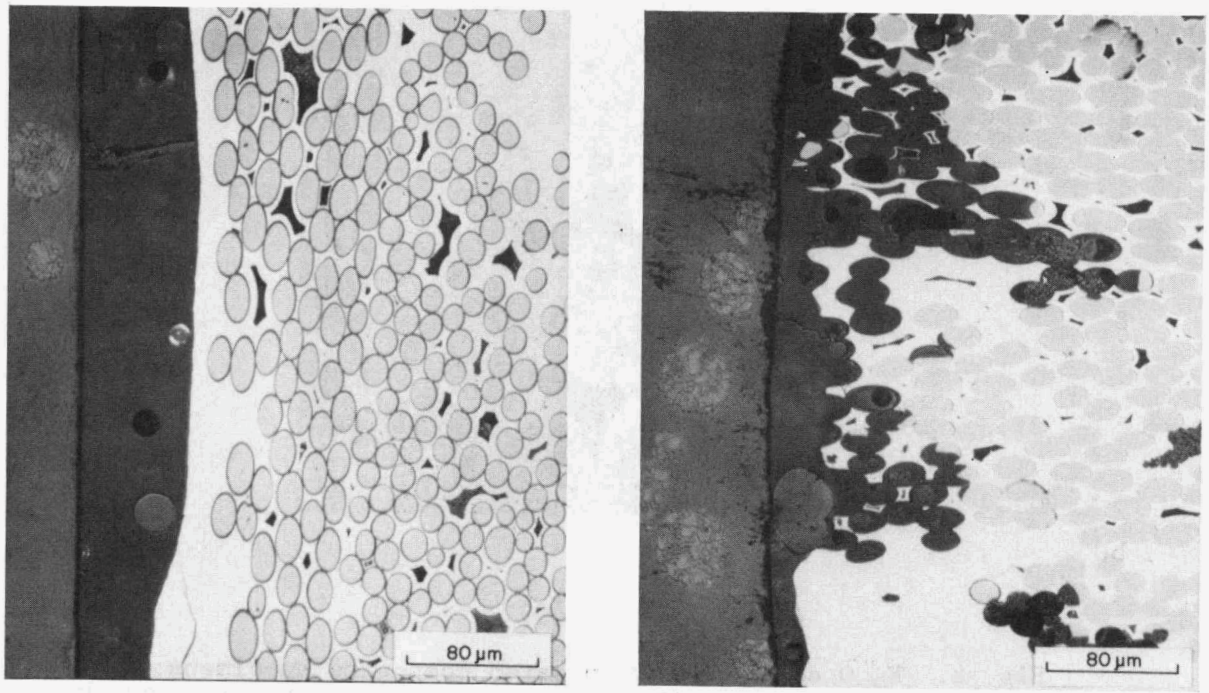


Fig. 9. An oxygen elemental map and sulfur line scan for an unprotected composite after 100-h exposure at 1273 K to the combustion of natural gas in air with 1% H_2S.

YP10737



(*a*) (*b*)

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

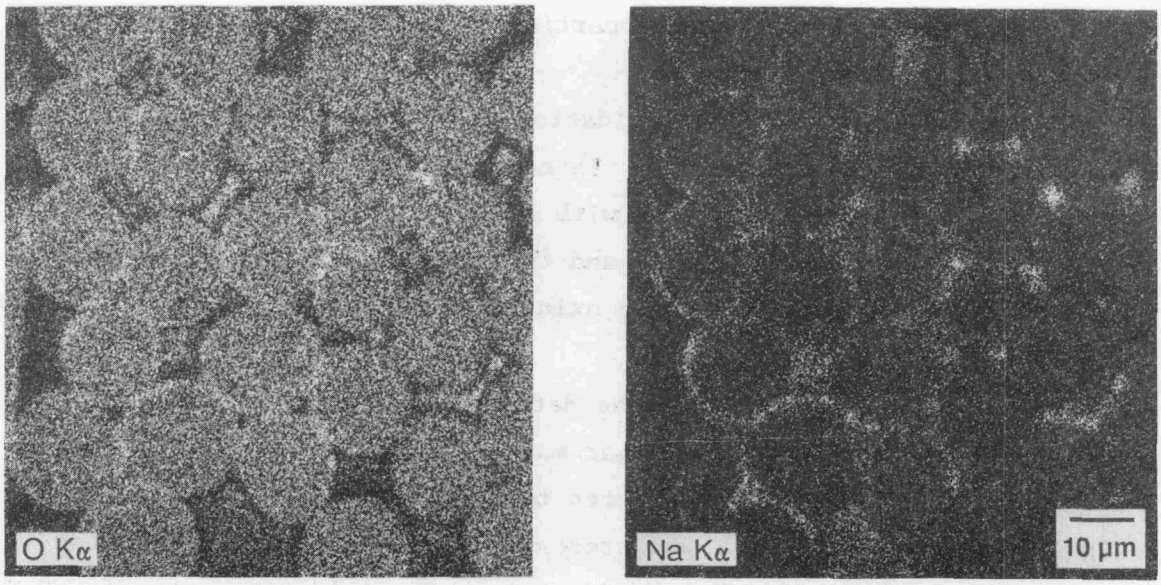


Fig. 11. Oxygen and sodium elemental maps for an unprotected composite after 100-h exposure at 1273 K to the combustion of natural gas in air with ≈ 80 ppm Na.

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 ≈ 10^{-3} g/cm^2-min, or about 5 μm/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, SiO_2, and C,[25,26] oxidize more rapidly than CVD SiC, thus producing a thicker SiO_2 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 not resistant to long-term attack by sodium at elevated temperatures.

6. ACKNOWLEDGMENTS

This research is sponsored by the U.S. Department of Energy, Fossil Energy AR&TD Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc. The author would like to thank the ORNL High Temperature Materials Laboratory User Center for the use of the Hitachi S-800 scanning electron microscope and access to the other analytical and mechanical property testing equipment. Special gratitude is extended to K. L. More for the TEM work and T. Henson for the electron microprobe analysis. Appreciation is also due P. Tortorelli and D. Wilson for review of the manuscript.

7. REFERENCES

1. Stinton, D. P., A. J. Caputo, and R. A. Lowden, "Synthesis of Fiber-Reinforced SiC Composites by Chemical Vapor Infiltration," *Am. Ceram. Soc. Bull.* **65**(2), 347-50 (1986).
2. Sambell, R. A. J., A. Briggs, D. C. Phillips, and D. H. Bowen, "Carbon Fiber Composites with Glass and Glass-Ceramic Matrices, Part 2: Continuous Fibers," *J. Mater. Sci.* 7, 676-81 (1972).
3. Prewo, K. M. and J. J. Brennan, "High-Strength Silicon Carbide Fiber-Reinforced Glass-Matrix Composites," *J. Mater. Sci.* **15**, 463-68 (1980).

4. Prewo, K. M., J. J. Brennan, and G. K. Layden, "Fiber-Reinforced Glasses and Glass-Ceramics for High Performance Applications," *Ceram. Bull.* **65**(2), 305-22 (1986).

5. Mah, T., M. G. Mendiratta, A.P. Katz, and K. S. Mazdiyasni, "Recent Developments in Fiber-Reinforced High Temperature Ceramic Composites," *Ceram. Bull.* **66**(2), 304-17 (1987).

6. Caputo, A. J., D. P. Stinton, R. A. Lowden, and T. M. Besmann, "Fiber-Reinforced SiC Composites with Improved Mechanical Properties," *Am. Ceram. Soc. Bull.* **66**(2), 268-72 (1987).

7. Budiansky, B., J. W. Hutchinson, and A. G. Evans, "Matrix Fracture in Fiber-Reinforced Ceramics," *J. Mech. Phys. Solids* 34(2), 167-89 (1986).

8. Lowden, R. A., *Characterization and Control of the Fiber-Matrix Interface in Ceramic Matrix Composites*, ORNL/TM-11039, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., March 1989.

9. Lowden, R. A., and K. L. More, "The Effect of Fiber Coatings on Interfacial Shear Strength and the Mechanical Behavior of Ceramic Composites," *MRS Symposium Proceedings, Vol. 170, Tailoring Multiphase and Composite Ceramics*, March 1989.

10. Brennan, J. J., "Interfacial Characterization of Glass and Glass-Ceramic Matrix/Nicalon SiC Fiber Composites," pp. 549-60 in *MRS Proceedings, Vol. 20, Tailoring Multiphase and Composite Ceramics*, ed. R. E. Tressler et al., Plenum Publishing Corporation, New York, 1986.

11. Besmann, T. M., R. A. Lowden, D. P. Stinton, and T. L. Starr, "A Method for the Rapid Chemical Vapor Infiltration of Ceramic Composites," *J. de Physique* **5**(50), Colloque C5, 229-39 (1989).

12. Hancock, P., "The Use of Laboratory and Rig Tests to Simulate Gas Turbine Corrosion Problems," *Corros. Sci.* **22**(1), 51-65 (1982).

13. Jacobson, N. S., C. A. Stearns, and J. L. Smialek, "Burner Rig Corrosion of SiC At 1000°C," *Adv. Ceram. Mater.* **1**(2), 154-61 (1986).

14. Besmann, T. M., *SOLGASMIX-PV, a Computer Program to Calculate Equilibrium Relationships in Complex Chemical Systems*, ORNL/TM-5775, Martin Marietta Energy Systems, Inc., Oak Ridge Natl. Lab., April 1977.

15. Tiearney, T. C., Jr., and K. Natesan, "Sulfidation-Oxidation of Advanced Metallic Materials on Simulated Low-Btu Coal Gasifier Environments," *Oxid. Met.* **17**(1/2), 1-25 (1982).

16. Yavorskii, I. A., V. I. Elchin, and G. G. Gnesin, "Reactions of Silicon Carbide with Oxidizing Atmospheres," *Sov. Powder Metall. Met. Ceram.* **17**, 542-45 (1978).

17. McKee, D. W., and D. Chatterji, "Corrosion of Silicon Carbide in Gases and Alkaline Melts," *J. Am. Ceram. Soc.* **59**(9-10), 441-44 (1976).

18. Federer, J. I., "Corrosion of SiC by Na_2SO_4," *Adv. Ceram. Mater.* **3**(1), 56-61 (1988).

19. Jones, R. H., C. H. Henager, Jr., P. P. Trzaskoma, N. S. Stoloff, T. P. Moffat, and B. D. Lichter, "Environmental Effects on Advanced Materials," *J. Met.* 19-30 (December 1988).

20. Hove, J. E., and W. C. Riley, "Graphite," pp. 14-76 in *Ceramics for Advanced Technologies*, John Wiley and Sons, New York, 1965.

21. Fretty, N. and M. Boussuge, "Relationship Between High-Temperature Development of Fiber-Matrix Interfaces and the Mechanical Behavior of SiC-SiC Composites," *Compos. Sci. Tech.* **37**, 177-89 (1990).

22. Menessier, E., A. Guette, R. Pailler, R. Naslain, L. Rabardel, B. Hosten, T. Macke, and P. Lespade, "Thermo-mechanical Characterization of Ceramic Composites Made of a LAS Glass-Ceramic Reinforced with Silicon Carbide Fibers," pp. 121-27 in *Proceedings of the Third European Conference on Composite Materials*, ed. A. R. Bunsell, P. Lamicq, and A. Massiah, Elsevier Applied Science, London, 1989.

23. Frisch, B., W. R. Thiele, R. Drumm, and B. Münnich, "On the Oxidation Mechanisms of Silicon Carbide in the 300 to 1300°C Temperature Range," *CFI/Ber.* **65**(8/9), 277-84 (1988).

24. Shiroky, G. H., "Oxidation Behavior of Chemically Vapor Deposited Silicon Carbide," *Adv. Ceram. Mater.* **2**(2), 137-41 (1987).

25. Fareed, A. S., P. Fang, M. Koczak, and F. Ko, "Thermochemical Properties of SiC Yarn," *Ceram. Bull.* **66**(2), 353-58 (1987).

26. Clark, T. J., M. Jaffe, J. Rabe, and N. R. Langley, "Thermal Degradation of Nicalon SiC Fibers," *Ceram. Eng. Sci. Proc.* **6**(7-8), 576-88 (1985).

INTERNAL DISTRIBUTION

1-2. Central Research Library
3. Document Reference Section
4-5. Laboratory Reference Section
6. Laboratory Records, ORNL RC
7. ORNL Patent Section
8-10. M&C Records Office
11. K. B. Alexander
12. R. L. Beatty
13. P. F. Becher
14. T. M. Besmann
15. P. J. Blau
16. T. D. Burchell
17. P. T. Carlson
18. N. C. Cole
19. D. F. Craig
20. J. H. DeVan
21. E. L. Fuller
22. C. Hsueh
23. A. R. Irvine
24. M. G. Jenkins
25. R. R. Judkins
26. M. A. Karnitz
27. J. R. Keiser
28. J. O. Kiggans
29-33. R. A. Lowden
34. R. C. Martin
35. A. J. Moorhead
36. O. O. Omatete
37. D. P. Stinton
38. P. F. Tortorelli
39. D. F. Wilson
40. S. J. Zinkle
41. A. D. Brailsford (Consultant)
42. Y. A. Chang (Consultant)
43. H. W. Foglesong (Consultant)
44. J. J. Hren (Consultant)
45. M. L. Savitz (Consultant)
46. J. B. Wachtman, Jr. (Consultant)

EXTERNAL DISTRIBUTION

47. ACUREX CORPORATION, 555 Clyde Avenue, P.O. Box 7555, Mountain View, CA 94039

    J. Sawyer

48. ADIABATICS, INCORPORATED, 630 S. Mapleton, Columbus, IN 47201

    R. Kamo

49-51. AFWAL/MLLM, Wright-Patterson AFB, OH 45433

    A. Katz
    L. Matson
    S. Szaruga

52-55. AIR PRODUCTS AND CHEMICALS, INC., P.O. Box 538T, Allentown, PA 18105

    P. N. Dyer
    V. L. Magnotta
    R. K. Malhotra
    S. V. Raman

56. AIRCO TEMESCAL, 2850 Seventh Street at Heinz, Berkeley, CA 94710

E. Demiray

57. AIRESEARCH MANUFACTURING COMPANY, 2525-T West 190th Street, Torrance, CA 90509

D. M. Kotchick

58. AMERCOM, INC., 8928 Fullbright Avenue, Chatsworth, CA 91311

W. E. Bustamante

59. ARCO CHEMICALS COMPANY, Silag Operation, Route 6, Box A, Greer, SC 29651

J. F. Rhodes

60. ARGONNE NATIONAL LABORATORY, 9700 South Cass Avenue, Argonne, IL 60439

W. A. Ellingson

61-62. ARMY MATERIALS AND MECHANICS RESEARCH CENTER, Arsenal Street, Watertown, MA 02172

R. N. Katz
J. W. McCauley

63. AVCO, 201 Lowell Street, Wilmington, MA 01887

T. Vasilos

64-67. AVCO SPECIALTY MATERIALS, 2 Industrial Avenue, Lowell, MA 01851

B. Belason
T. F. Foltz
W. Foulds
J. F. Lacouste

68-71. BABCOCK & WILCOX COMPANY, Lynchburg Research Center, P.O. Box 239, Lynchburg, VA 24505

L. J. Ferrell
W. G. Long
H. H. Moeller
D. R. Petrak

72-73. BATTELLE COLUMBUS LABORATORIES, 505 King Avenue, Columbus, OH 43201

S. P. Mukherjee
I. G. Wright

74-77. BATTELLE PACIFIC NORTHWEST LABORATORIES, P.O. Box 999, Battelle Boulevard, Richland, WA 99352

T. D. Chikalla
E. Courtwright
S. D. Dahlgren
E. McClanahan

78. CABOT CORPORATION, 125 High Street, Boston, MA 02110

N. Fiore

79-81. CATERPILLAR TRACTOR COMPANY, Peoria, IL 61629

M. B. Beardsky
M. Haselkorn
G. G. Volbert

82-83. CERAMATEC, INC., 163 West 1700 Street, Salt Lake City, UT 84115

C. W. Griffin
D. W. Richerson

84-88. CLEMSON UNIVERSITY, Clemson, SC 29632

R. D. James

89. COMURHEX, INC., Usine de Pierrelatte, B.P. 29 - 26701 Pierrelatte, Cedex, France

D. Gaillard

90-93. CORNING GLASS WORKS, Corning, NY 14831

K. Chyung
R. C. Doman
D. C. Larson
P. Papa

94-96. CUMMINS ENGINE COMPANY, INC., 1000 5th St., Columbus, IN 47201

J. W. Patten
G. L. Starr
T. M. Yonushonis

97-100. E. I. DUPONT DE NEMOURS & COMPANY, INC., Experimental Station 302/22, Wilmington, DE 19898

P. Geoghegan
C. Lundgren
J. Morris
J. C. Romine

101. ENGELHARD CORPORATION, Menlo Park, CN 28, Edison, NJ 08818

A. Mishra

102-103. FORD MOTOR COMPANY, Engineering and Research, P.O. Box 2053, Dearborn, MI 48121

D. L. Hartsock
A. F. McLean

104-105. GENERAL ATOMICS, P.O. Box 81608, San Diego, CA 92138

T. D. Gulden
K. S. Mazdiyasni

106. GENERAL MOTORS CORPORATION, Allison Gas Turbine Operations, Low Heat Rejection Diesel Technology, P.O. Box 420, Indianapolis, IN 46206

H. E. Helms

107-108. GEORGIA INSTITUTE OF TECHNOLOGY, 225 North Avenue, Atlanta, GA 30332

W. J. Lackey
T. L. Starr

109-111. GTE LABORATORIES, INC., 40 Sylvan Road, Waltham, MA 02254

M. L. Huckabee
A. E. Pasto
V. Sarin

112. HUGHES AIRCRAFT COMPANY, P.O. Box 902, 2000 East El Segundo Boulevard, El Segundo, CA 90245

M. Gardos

113. KAMAN SCIENCES CORPORATION, 1500 Garden of the Gods Road, P.O. Box 7463, Colorado Springs, CO 80933

J. L. Carr

114-115. KENNAMETAL, INC., P.O. Box 231, Latrobe, PA 15650

D. Kropful
E. J. Oles

116. KRW ENERGY SYSTEMS, P.O. Box 158, Madison, PA 15663

C. A. Andersson, Jr.

117-119. LANXIDE CORPORATION, Tralee Industrial Park, Newark, DE 19711

V. Irick, Jr.
M. Newkirk
A. W. Urquhart

120-122. LAWRENCE BERKELEY LABORATORY, University of California, P.O. Box 808, 1 Cyclotron Road, Berkeley, CA 94720

D. H. Boone
A. G. Evans
A. V. Levy

123-125. LOS ALAMOS NATIONAL LABORATORY, P.O. Box 1663, Los Alamos, NM 87545

F. D. Gac
G. F. Hurley
J. J. Petrovic

126. MAN TECHNOLOGIE GmbH, Postfach 50 04 26, Dachauer Strasse 667, D-8000 Munchen 50, Federal Republic of Germany

A. Muehlratzer

127-128. MARTIN MARIETTA LABORATORIES, 1450 South Rolling Road, Baltimore, MD 21227

D. C. Nagle
A. R. C. Westwood

129-130. MASSACHUSETTS INSTITUTE OF TECHNOLOGY, Cambridge, MA 02139

H. K. Bowen
J. S. Haggerty

131-132. MECHANICAL TECHNOLOGY, INC., 968 Albany-Shaker Road, Latham, NY 12110

W. F. Bessler
M. Schreiner

133. NASA-LANGLEY RESEARCH CENTER, MS 188-B, Hampton, VA 23665

D. R. Tenney

134-139. NASA-LEWIS RESEARCH CENTER, 21000 Brookpark Road, Cleveland, OH 44135

C. C. Berndt
D. H. Buckley
S. R. Levine
T. J. Miller
H. B. Probst
H. Sliney

140. NATIONAL ACADEMY OF SCIENCES, National Materials Advisory Board, Washington, DC 20418

R. M. Spriggs

141-142. NATIONAL INSTITUTE OF STANDARDS AND TECHNOLOGY, 562 Fracture and Deformation, Gaithersburg, MD 20899

E. R. Fuller
S. M. Wiederhorn

143. NATIONAL RESEARCH COUNCIL OF CANADA, 1411 Oxford Street, Halifax, N.S., Canada B3H3Z1

K. J. Konsztowicz

144-145. NORTH CAROLINA STATE UNIVERSITY, Department of Materials Engineering, P.O. Box 5427, 232 Riddick Laboratory, Raleigh, NC 27607

H. Conrad
R. F. Davis

146. NORTH CAROLINA STATE UNIVERSITY, P.O. Box 5995, Raleigh, NC 27607

H. Palmour III

147. OAK RIDGE ASSOCIATED UNIVERSITIES LIBRARY, Oak Ridge, TN 37831

MERT Division

148. OHIO STATE UNIVERSITY, 2041 College Road, Columbus, OH 43210

D. Readey

149-150. PENNSYLVANIA STATE UNIVERSITY, Materials Engineering Research Laboratory, 201 Steidle Building, University Park, PA 16802

K. Spear
R. E. Tressler

151-153. PRATT & WHITNEY AIRCRAFT, 400 Main St., East Hartford, CT 06108

O. Chen
C. S. Giggins
D. L. Ruckle

154. REFRACTORY COMPOSITES, INC., 12220-A Rivera Road, Whittier, CA 90606

E. Paquette

155. ROCKWELL INTERNATIONAL, 1049 Camino Dos Rios, P.O. Box 1085, Thousand Oaks, CA 91360

P. E. D. Morgan

156. SAN FERNANDO LABORATORIES, 10258 Norris Avenue, Pacoima, CA 91331

R. A. Holzl

157. SANDIA NATIONAL LABORATORIES, P.O. Box 5800, Albuquerque, NM 87115

D. Maddox

158. R. L. Smith, P.O. Box 98, Chassel, MI 49916

159. TECHNOLOGY ASSESSMENT AND TRANSFER COMPANY, 9607 Muirfield Drive, Upper Marlboro, MD 20772

L. L. Fehrenbacher

160. 3M COMPANY, 3M Center, 218-35-04, St. Paul, MN 55144

R. E. Richards

161. UNION CARBIDE CORPORATION, Market Development, Carbon Products Division, P.O. Box 6087, Cleveland, OH 44101

M. B. Dowell

162. U.S. ARMY TANK-AUTOMOTIVE COMMAND (TACOM), R&D Center, Warren, MI 48090

P. C. Glance

163. U.S. DEPARTMENT OF DEFENSE, Advanced Research Projects Agency, 1400 Wilson Boulevard, Arlington, VA 22209

B. F. Wilcox

164-165. UNITED TECHNOLOGIES RESEARCH CENTER, Silver Lane, MS 24, East Hartford, CT 06108

J. J. Brennan
K. Prewo

166. UNIVERSITY OF TENNESSEE, Department of Materials Science, Knoxville, TN 37996

J. E. Spruill

167. UNIVERSITY OF WASHINGTON, Seattle, WA 98195

R. C. Bradt

168. VIRGINIA POLYTECHNIC INSTITUTE AND STATE UNIVERSITY, Blacksburg, VA 24061

D. P. H. Hasselman

169. VOUGHT CORPORATION, MSTH 83, P.O. Box 225907, Dallas, TX 75265

H. F. Volk

170-171. W. R. GRACE & COMPANY, 7379 Route 32, Columbia, MD 21044

W. R. Rice
J. P. Skalny

172. WESTINGHOUSE ELECTRIC CORPORATION, Research and Development Center, 1310 Beulah Road, Pittsburgh, PA 15235

R. J. Bratton

173-174. WILLIAMS INTERNATIONAL CORPORATION, 2280 West Maple Road, Walled Lake, MI 48088

W. Chapman
P. Nagy

175-183. DOE, MORGANTOWN ENERGY TECHNOLOGY CENTER, P.O. Box 880, Morgantown, WV 26505

R. A. Bajura
R. C. Bedick
D. C. Cicero
F. W. Crouse, Jr.
N. T. Holcombe
W. J. Huber
M. J. Mayfield
J. E. Notestein
J. S. Wilson

184. DOE, OFFICE OF BASIC ENERGY SCIENCES, Division of Materials Sciences, ER-131, GTN, Washington, DC 20585

J. B. Darby

185. DOE, OFFICE OF CONSERVATION AND RENEWABLE ENERGY, CE-12 Forrestal Building, Washington, DC 20545

J. J. Eberhardt

186-187. DOE, OFFICE OF ENERGY SYSTEMS RESEARCH, Washington, DC 20585

J. J. Eberhardt
S. M. Wolf

188-190. DOE, OFFICE OF FOSSIL ENERGY, FE-14, Mail Stop B127, GTN, Washington, DC 20585

D. J. Beecy (FE-14) GTN
J. P. Carr (FE-14) GTN
F. M. Glaser (FE-14) GTN

191. DOE, OFFICE OF INDUSTRIAL PROGRAMS, Washington, DC 20585

S. L. Richlen

192-193. DOE, OFFICE OF TRANSPORTATION TECHNOLOGIES, Washington, DC 20585

A. A. Chesnes
R. B. Schulz

194-197. DOE, PITTSBURGH ENERGY TECHNOLOGY CENTER, P.O. Box 10940, Pittsburgh, PA 15236

A. H. Baldwin
G. V. McGurl
R. Santore
T. M. Torkos

198. DOE FIELD OFFICE, OAK RIDGE, P.O. Box 2001, Oak Ridge, TN 37831-8600

Assistant Manager for Energy Research and Development

199. DOE FIELD OFFICE, OAK RIDGE, Oak Ridge National Laboratory, P.O. Box 2008, Building 4500N, MS 6269, Oak Ridge, TN 37831-6269

E. E. Hoffman

200-209. DOE, OFFICE OF SCIENTIFIC AND TECHNICAL INFORMATION, Office of Information Services, P.O. Box 62, Oak Ridge, TN 37831

For distribution by microfiche as shown in DOE/OSTI-4500, Distribution Categories UC-103 (Fluidized Bed Combustion), UC-105 (Flue Gas Cleanup), UC-106 (Gas Stream Cleanup), UC-108 (Coal Liquefaction), UC-109 [Coal Gasification (Surface and Underground)], UC-110 (Fuel Cells), UC-111 (Heat Engines), and UC-114 (Coal Based Materials and Components)