CONF-960106-

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STRESS-TEMPERATURE-LIFETIME RESPONSE OF NICALON FIBER-REINFORCED SIC COMPOSITES IN AIR

REFERENCE: Lin, H.-T., Becher, P. F., **"Stress-Temperature-Lifetime Response of *Nicalon Fiber-Reinforced SiC Composites* in Air,"** Thermal and Mechanical Test Methods and Behavior of Continuous-Fiber Ceramic Composites, ASTM STP 1309, Michael G. Jenkins, Stephen T. Gonczy, Edgar Lara-Curzio, Noel E. Ashbaugh, Larry P. Zawada, Eds., American Society for Testing and Materials, Philadelphia, 1996.

ABSTRACT: Time-to-failure tests were conducted in four-point flexure and in air as a function of stress levels and temperatures to study the lifetime response of various Nicalon fiber-reinforced SiC (designated as Nic/SiC) composites with a graphitic interfacial coating. The results indicated that all of the Nic/SiC composites exhibit a similar stress-dependent failure at applied stress greater than a threshold value. In this case, the lifetimes of the composites increased with decrease in both stress level and test temperature. The lifetime of the composites appeared to be relatively insensitive to the thickness of graphitic interface layer and was enhanced somewhat by the addition of oxidation inhibitors. Electron microscopy and oxidation studies indicated that the life of the Nic/SiC composites was governed by the oxidation of the graphitic interfaces and the formation of glass(es) in composites due to the oxidation of the fiber and matrix, as well as any inhibitor phases.

KEYWORDS: Nicalon fiber, SiC matrix, Nic/SiC composite, static fatigue, CFCC

Reinforcement by continuous fibers can substantially improve the damage tolerance of ceramics by bringing about the fiber debonding, fiber bridging, and fiber pull out processes. Such toughening mechanisms are achieved through the introduction of an interface/fiber coating. A weakly bonded interfacial layer is often used to obtain fiber debonding from the matrix. As a result, continuous fiber-reinforced ceramic composites

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(CFCCs) exhibit relatively large strains to failure with high toughness values, which are in sharp contrast to the monolithic ceramics that exhibit brittle, catastrophic fracture behavior.

Continuous Nicalon fiber-reinforced SiC matrix composites fabricated by chemical vapor infiltration (CVI) process are candidates for high-temperature structural applications, due to their attractive mechanical performance at room and elevated temperatures [1-7]. These structural applications include radiant burners, hot gas filters, high-pressure heat exchanger tubes, and industrial gas turbine engines. Because of its strong anisotropic microstructure and its role in protecting fibers during processing, a graphitic fiber coating has been applied to facilitate interfacial debonding and fiber pullout. However, graphite oxidizes readily at temperatures above 400°C in air [8]. The mechanical performance and long-term reliability of Nic/SiC composites is, therefore, a concern under applied stresses at elevated temperatures in an oxidizing environment.

It was previously shown that the air exposure at 950°C could cause a substantial degradation in a Nic/SiC composite with a 0.3 μm graphitic fiber coating in the absence of outer SiC seal coating [9]. In that study, no external applied stress was used during elevated temperature air exposure. A separate study showed that in the absence of applied stress a Nic/SiC composite with an external SiC seal coat exhibited no strength degradation after a 1000 h air exposure at 1000°C [10]. However, the presence of a static flexural loading during air exposure at 950°C could promote failure of a Nic/SiC composite with a 50-100 nm graphite coating [11]. Furthermore, a static fatigue study in flexure conducted by Lin *et al.* [12] has shown that a Nic/SiC composite with a 0.3 μm graphitic fiber coating and without an outer seal coating exhibited stress-dependent lifetimes when the applied stresses were above a threshold value, which was similar to the proportional limit of this composite. The time to failure decreased with increasing the applied stress level and test temperature. The results also revealed that a SiC seal coat played little protective function at 950°C in air [12]. The fatigue study conducted by Lin *et al.* indicated that the lifetimes of the Nic/SiC composite above the threshold stress was controlled by the oxidation of the graphitic interfacial layer and fibers.

At present, only a very limited database is available to provide some insight into the effect of stress, temperature, and environment on the lifetimes of Nic/SiC composites. As a part of the research efforts in CFCC program [13], the current task is studying the effect of applied flexural stress on the lifetime response of various Nic/SiC composites at temperatures up to 1200°C in air. The current experiments at temperatures of 600° and 950°C were designed to investigate the temperature range over which oxidation effects can alter the mechanical performance and, thus, the reliability of Nic/SiC composites with a graphitic interface. The effects of modifications in the fiber coating thickness, composite density, and the chemical composition of the matrix were also evaluated.

EXPERIMENTAL PROCEDURES

Time-to-failure studies as functions of applied stress and temperature were conducted in air on several commercially available Nic/SiC composites (designated as Composite A, B, C, and D). The general microstructures of the as-received composites are shown in Figure 1. The A and B commercial composites were produced by infiltrating a lay-up of 0°/90° Nicalon plain weave cloth (Nippon Carbon Company, Tokyo, Japan) with SiC matrix by CVI; each composite utilized a carbon fiber coating to facilitate interfacial debonding and fiber pullout. Composite A contains ~ 43 vol. % fibers with a carbon interfacial layer 0.5 to 0.7 μm thick, exhibits ~ 25 vol. % open porosity, and was tested with as-machined surface. In addition, Composite A exhibits a banded or agate-like structure in both the darker outer layer and the CVI SiC matrix (Fig. 1a). Matrix cracks are also frequently associated with this distinct banding in the matrix. This agate-like banding is not apparent in other Nic/SiC composites investigated in the present study (Fig. 1). The dark phase was found to be enriched with boron content (10 to 20 at. %). Composite B also contains ~ 43 vol. % fibers with a carbon interfacial layer ~ 0.05-0.1 μm thick, less (~ 17 vol. %) open porosity, and has an external layer of CVD SiC seal coating ~ 40 μm thick.

Composites C and D were also produced by infiltrating a lay-up of 0°/90° Nicalon plain weave cloth with SiC matrix by CVI. Both Composite C and D contain a mixture of carbon plus particulate fillers, as an oxidation inhibitor, to coat the fiber bundles prior to the final CVI of SiC (Fig. 1c). The mixture of carbon and particulate oxidation inhibitors were introduced via proprietary impregnation and carbonization processes. Auger analysis of the oxidation inhibitors indicated boron and carbon. In addition to the introduction of a mixture of carbon and oxidation inhibitor, Composite D contains an additional coating, i.e., oxide phase plus particulate inhibitors, between the fiber cloths for further improvement of the performance at elevated temperatures in air (Fig. 1d). Auger analysis of the oxide phase indicated silicon, carbon, and oxygen. Both Composite C and D contain ~ 43 vol. % fibers, exhibit ~ 15 vol. % open porosity, and have an external layer of CVD SiC seal coat ~ 50 μm thick. Thus, Composites A to D all differ from the previously investigated ORNL Nic/SiC composite in terms of matrix composition, interfacial coating thickness and fiber cloth lay-up [12]. This Nic/SiC composite, manufactured at Oak Ridge National Laboratory (ORNL), consisted of a CVI SiC matrix and ~ 43 vol. % Nicalon fibers in the form of plain weave cloth with the cloth layers rotated 30° between layers. The fiber in the Nicalon cloth had a 0.3 μm graphite coating, which was deposited prior to infiltration of the SiC matrix.

The dimensions of bend bars prepared from Composite A and B were 3 mm x 4 mm x > 50 mm, whereas for Composite C and D the dimensions were 2.5 mm x 6.6 mm x > 50 mm. The 0° fibers in the test bend bars were in an orientation parallel to the tensile stress direction. The static fatigue in four point bending was conducted at temperatures of 600° and 950°C in air. The test fixtures were fabricated from sintered α-SiC with inner and outer spans of 20 and 40 mm, respectively. A pneumatic type loading system was used to applied the load to the test bend bars through an alumina pushrod. The test bars were

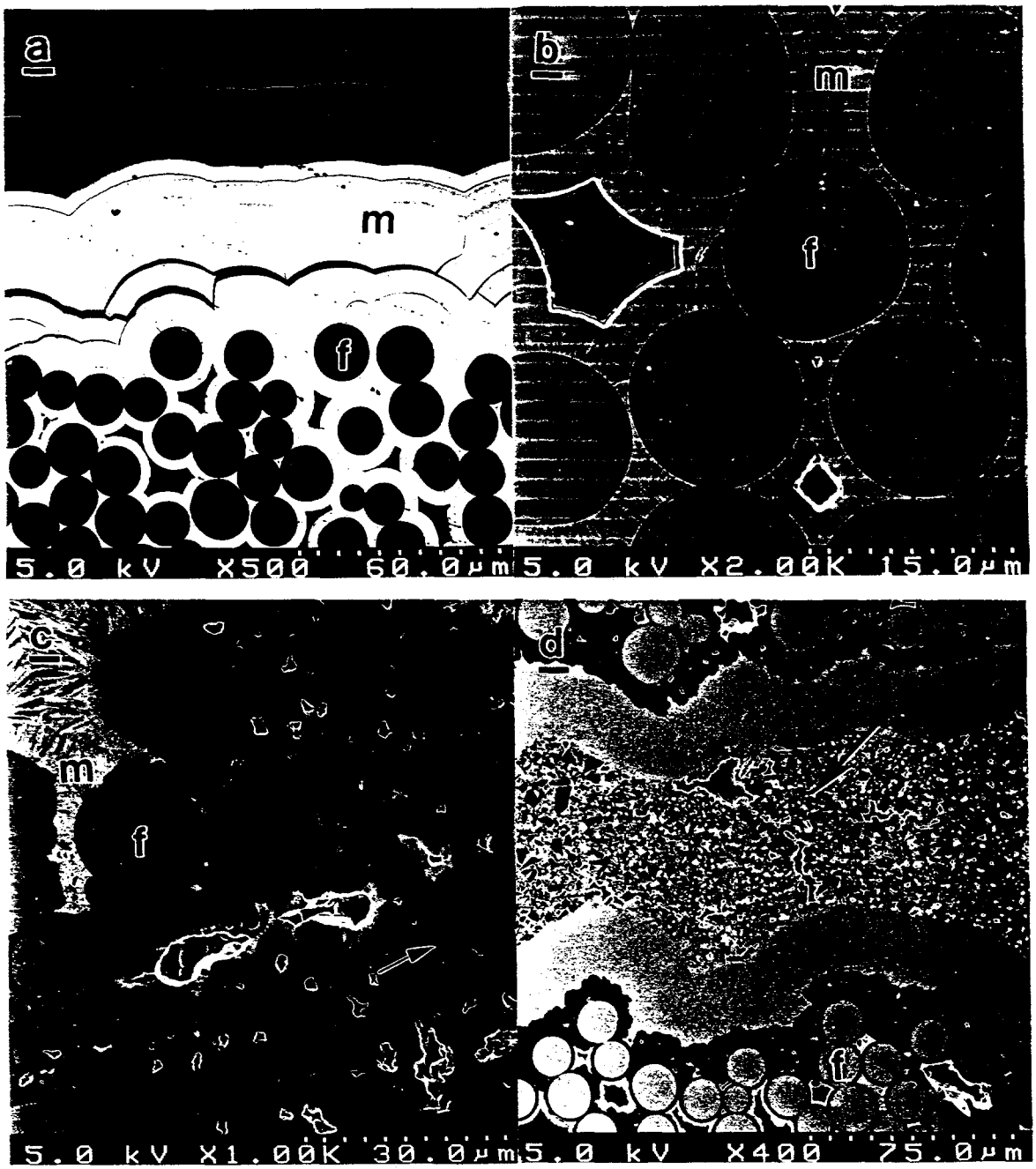

FIG. 1. General microstructures of as-received Nic/SiC composites. (a) Composite A with a 0.5-0.7 µm thick interface accompanied by a banded structure in the matrix, (b) Composite B with a 0.05-0.10 µm thick interface, (c) Composite C with a mixture of graphite and oxidation inhibitors, and (d) Composite D with an additional oxide plus oxidation inhibitors coating. The labels of "f" and "m" denote the fiber and matrix, respectively. The arrows indicate the inhibitors in (c) and additional coating in (d).

held in the fixture with a small load (< 15 MPa outer fiber tensile stress) and heated to the desired test temperature and allowed to equilibrate for at least 30 minutes prior to increasing applied stress to the selected level. The applied stress was held constant (± 0.2 MPa deviation) until the test bar failed; at that point sensors interrupted the furnace power supply circuit to allow the bend bars to cool quickly to minimize damage and oxidation of the fracture surface. Optical and scanning electron microscopy (SEM) were used to characterize the microstructure of the as-received composites and the high temperature fracture surfaces as a function of stress level and test temperature.

RESULTS AND DISCUSSION

High Temperature Static Fatigue Behavior

Figure 2 shows the static fatigue results for Composites A and ORNL Nic/SiC composite at temperatures of 600° and 950°C under selected stress levels in air. The results of ORNL composite reported previously are included as a reference [12]. The results in Fig. 2 indicated that Composite A exhibited a limited structural capability at 950°C with an apparent fatigue limit of ~ 60 MPa, possibly due to its high open porosity (~ 25%) as compared to the rest of Nic/SiC composites investigated in the current and previous studies [12]. The results for the ORNL composite without seal coat showed that the mechanical performance degradation increased with the open porosity after exposure to air at 950°C for 50 h [14]. This was attributed to greater oxidation effects as the open porosity affords greater access of the air to the graphitic interface coating and fibers. In addition, the presence of matrix cracks in Composite A would further enhance the ingress of oxygen and the oxidation reaction.

The performance of Composite A at 600°C improved significantly and its performance was comparable to that of the ORNL composite at applied stresses < 200 MPa. Again, the low-stress carrying capability for Composite A was due to its high open porosity. While Composite A and ORNL composite were tested without a SiC seal coat, this is not considered likely to be a significant factor in tests employing applied stresses greater than the proportional limit at temperatures ≥ 600°C. Additional studies conducted on the ORNL composite and Composite A indicated that the seal coat provided minor or no improvement in lifetimes at temperatures of 600° and 950°C and at an applied stress above the proportional limit [12,15].

Figure 3 summarizes the fatigue results of Composite B and the ORNL composite at temperatures of 600° and 950°C in air. In spite of the differences in interface thickness and fiber layout, the density (open porosity) and fiber content in these two composites were similar. Note that both composites were tested with an external SiC coating. The data indicated that both Composite B and the ORNL composite exhibited similar lifetime response at both 600° and 950°C under the test conditions employed. These results suggests that the lifetime response of Nic/SiC composites with a graphitic interface

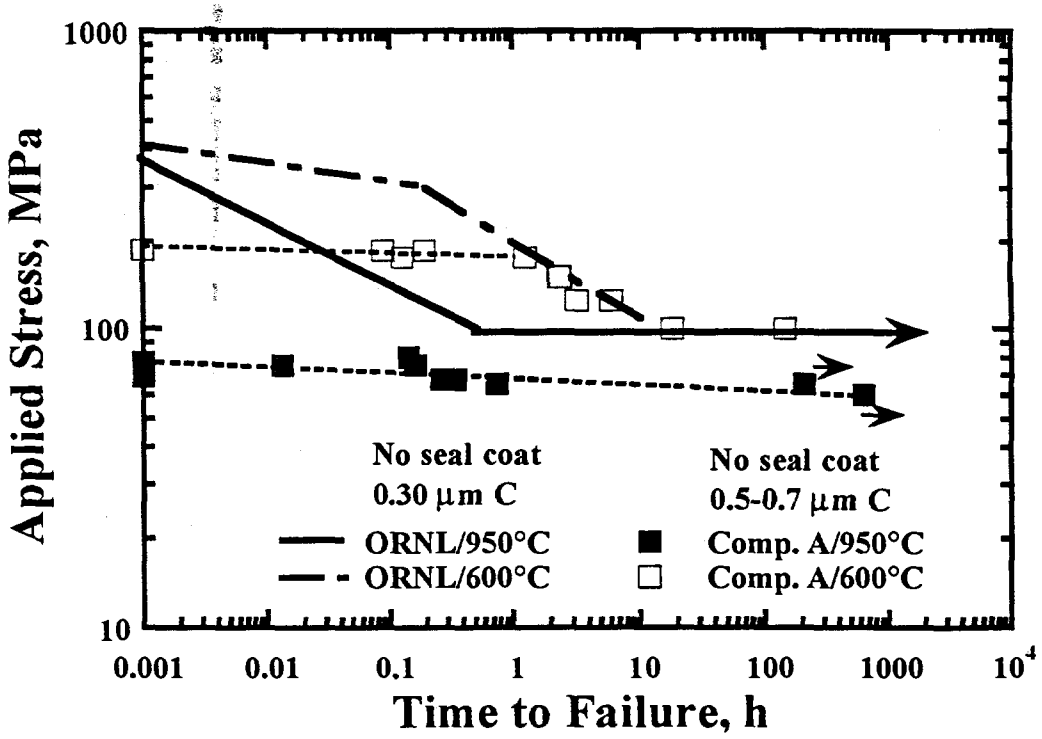

FIG. 2. Stress versus time to failure curves for composite A and the ORNL composite tested at 600° and 950°C in air.

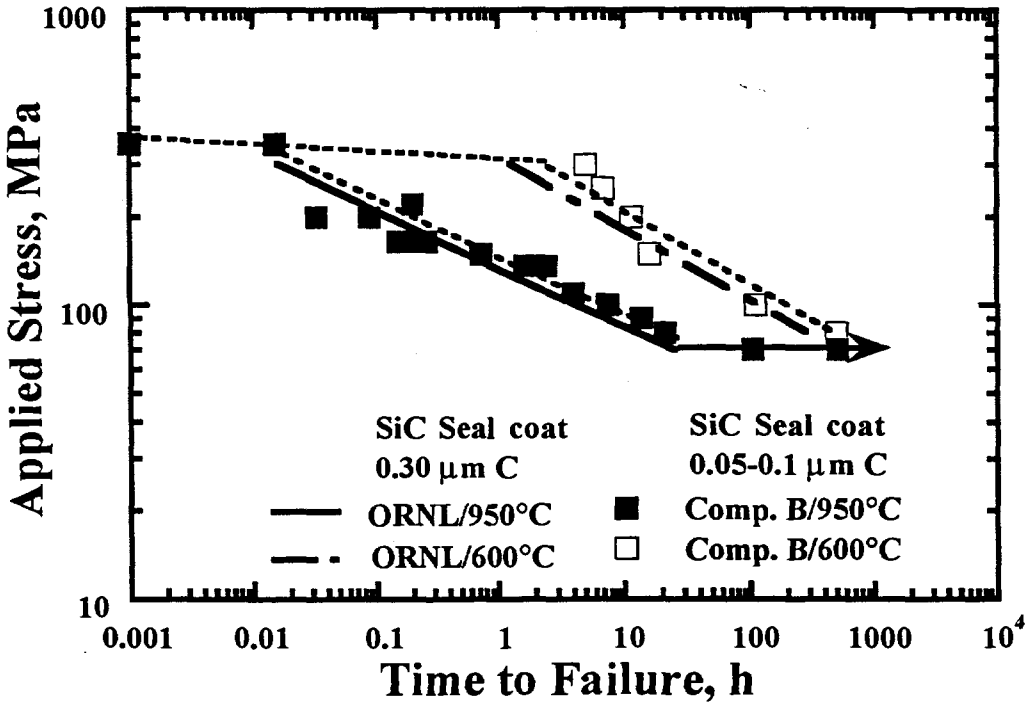

FIG. 3. Stress versus time to failure curves for Composite B and the ORNL composite tested at 600° and 950°C in air.

appears to be relatively insensitive to the interface thickness and fiber cloth lay-up for a similar open porosity. In addition, Composite B exhibited an apparent fatigue limit of ~ 70 MPa, which was lower than that obtained for the ORNL composite (~ 90 MPa). The variation in the fatigue limit between Composite B (70 MPa) and ORNL composite (90 MPa) may arise from the difference in fiber cloth lay-up.

Figures 4 and 5 show the time to failure results obtained for the Composite C and D and ORNL composite tested at temperatures of 600° and 950°C in air. The data showed that Composite C and D exhibited basically identical fatigue behavior under the test conditions employed (Fig. 5). The results suggest that the introduction of a coating, which consists of a mixture of an oxide phase and oxidation inhibitors, between fiber cloths in composite D does not provide any improved protective function under the applied stress level and test temperature range employed. Static fatigue data (Fig. 4) also showed that Composites C and D exhibited lifetimes, which were ~ 20-fold longer than the ORNL composite at temperatures of 600° and 950°C in air and at an applied stress above the apparent fatigue limit. In spite of differences in matrix microstructure and fiber lay-up, Composite C and D exhibited a similar fatigue limit to that obtained for the ORNL composite (~ 90 MPa). The enhancement in fatigue life of both Composite C and D is presumably due to the addition of boron-containing oxidation inhibitors. The presence of oxidation inhibitors, a glass former, could react with ingress oxygen to form a boron-containing glass that could seal the cracks generated in the matrix and retard the oxidation process, resulting in longer lifetimes. Nonetheless, at applied stress above the fatigue limit (> 90 MPa) the fatigue life of Composite C and D was still limited to < 300 h, which was only observed at 600°C.

Fatigue Damage Characterization

Previous static fatigue studies of the ORNL Nic/SiC composite with a graphitic interfacial layer indicated that the life limiting process at elevated temperatures under stress levels above the fatigue limit was associated with removal of the interfacial layer accompanied by the oxidation of fibers and matrix [12]. The Nic/SiC composites investigated in the present study contained graphitic interface layers with various thickness. It is, therefore, reasonable to anticipate that similar governing processes would occur in all the Nic/SiC composites investigated. Figure 6a shows a brittle surface feature with no fiber pullout in the tensile surface region for Composite B (with a 50-100 nm graphitic interfacial layer) tested at 950°C under an applied stress of 100 MPa in air. Depending upon the applied stress level and test temperature, the size of the brittle zone could vary between 50 to 80 % of the specimen cross section area. Occasionally, the presence of residual interfacial graphite with limited fiber pullout could be observed in both tensile and compressive region for Nic/SiC composites tested at 600°C with a short fatigue life (e.g., < 6 h), as shown in Fig. 6b. Similar fracture surface features as functions of stress and test temperature were also observed for Composite A and the ORNL composite [12]. At low temperatures (≤ 600°C), the oxidation of graphite was the

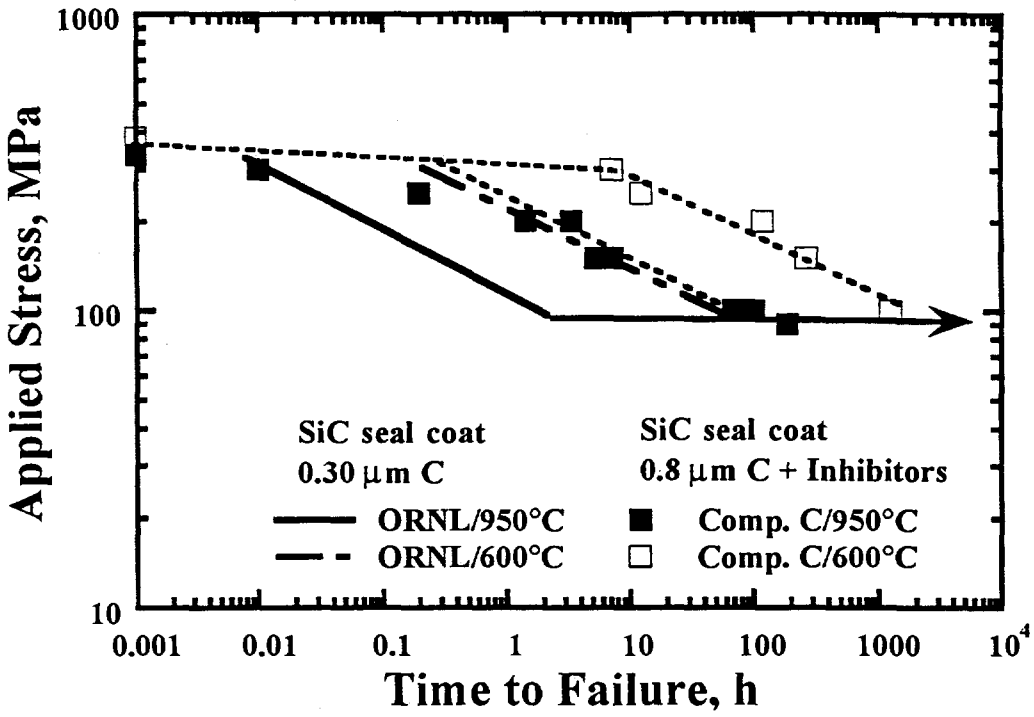

FIG. 4. Stress versus time to failure curves for Composite C and the ORNL composite tested at 600° and 950°C in air.

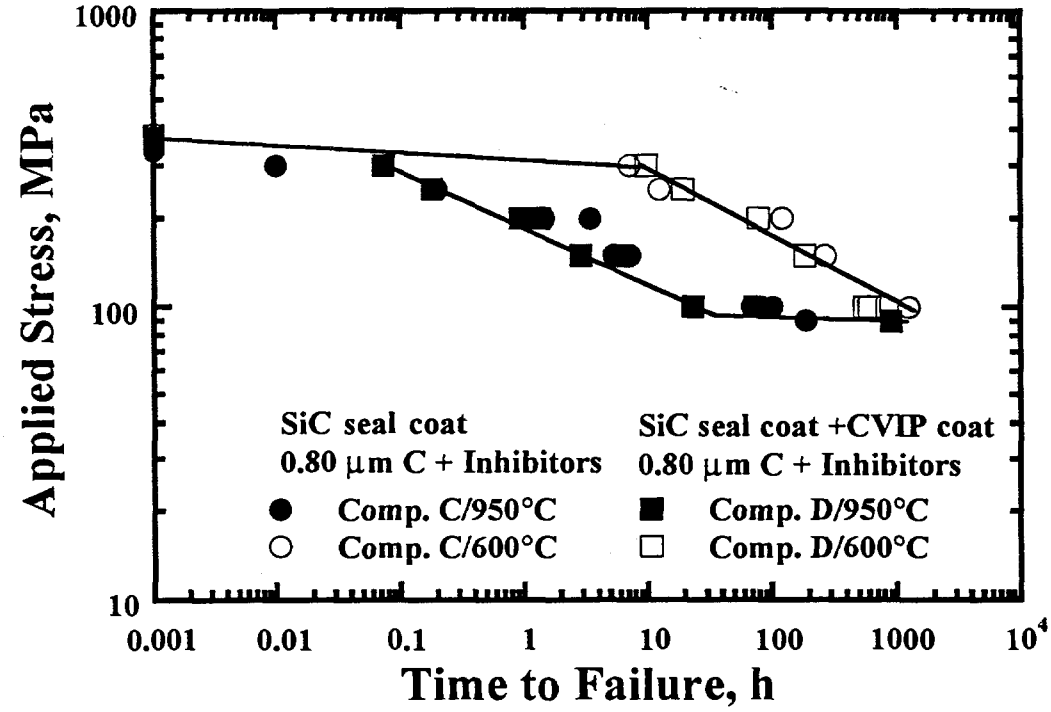

FIG. 5. Stress versus time to failure curves for Composite C and D tested at 600° and 950°C in air.

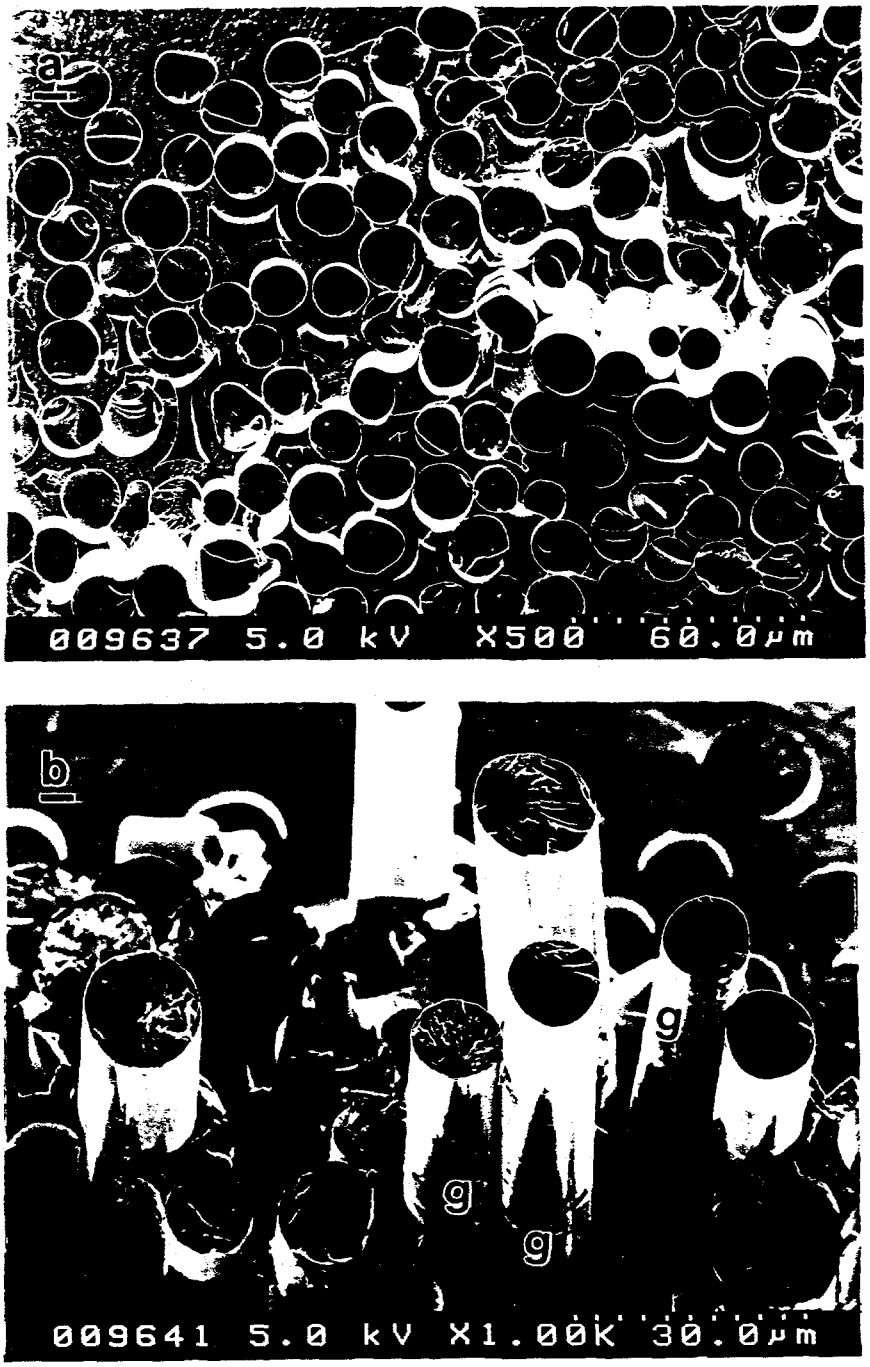

FIG. 6. Fracture surface features of Composite B tested at (a) 950°C showing brittle fracture, and (b) 600°C showing limited fiber pullout with residual graphite.

primary process detected by Thermogravimetric Analysis studies [16]. However, oxidation of the Nicalon fibers was also observed by Transmission Electron Microscopy examination in the ORNL Nic/SiC tested at 425°C in air [17]. In this case, the strength of the Nicalon fibers will continuously decrease with time due to oxidation reaction. The final failure occurs as the applied stress exceeds the residual fracture strength of the composite.

In Composite C and D, the particulate oxidation inhibitors were mixed with a graphite precursor and subsequently applied to the fiber cloths prior to final SiC infiltration. Both carbon and boron-containing inhibitors are known to exhibit measurable oxidation rates at temperatures ≥ 400°C in air [8,18,19]. Figure 7a shows a representative fracture surface in the tensile surface region of Composite C tested at 950°C/100 MPa with life of ~ 100 h. SEM observations revealed a substantial formation of boron-containing glass, due to the oxidation of particulate inhibitors, with no fiber pullout (brittle fracture). The amount of glass formation decreased with an increase in applied stress level and a decrease in test temperature. On the other hand, sponge-like graphite due to oxidation reaction was also observed within the fiber bundles in both the tensile and compressive regions (Fig. 7b). Oxidation and volatilization of particulate inhibitors [19] also occurred upon exposure to air leaving particulate-shaped pores on the surface (as seen in Fig. 7b). Oxidation of the mixture of graphite and particulate inhibitors within the fiber bundle will cause disintegration of the composite and lead to a continuous decrease in composite strength, resulting in a catastrophic failure. Fatigue results in the present study suggest that various matrix modifications, which were applied to the Nic/SiC composites investigated, can enhance the lifetime response somewhat but further improvement in the Nic/SiC composites is needed to meet the requirements for very extended lifetime over a wide range of temperature.

SUMMARY

Static fatigue tests in flexure were conducted to study the lifetime response of four commercial Nic/SiC composites with a graphitic interfacial coating as a function of applied stress at temperatures of 600° and 950°C in air. The static fatigue results indicated that all of the Nic/SiC composites, in spite of differences in interface thickness and matrix composition, exhibited similar stress-dependent failure at applied stress above the apparent fatigue limit. The lifetimes of Nic/SiC composites in an oxidizing environment increased with a decrease in both stress level and test temperature. The lifetime of Nic/SiC composites appeared to be relatively insensitive to the interface thickness and fiber cloth lay-up. The fatigue life was also somewhat enhanced by an introduction of particulate oxidation inhibitors. Electron microscopy and oxidation studies indicated that the fatigue life of the Nic/SiC composites investigated was governed by oxidation of the graphitic interface and the formation of glass(es) in the composite due to the oxidation of the fiber and matrix and any oxidation inhibitors.

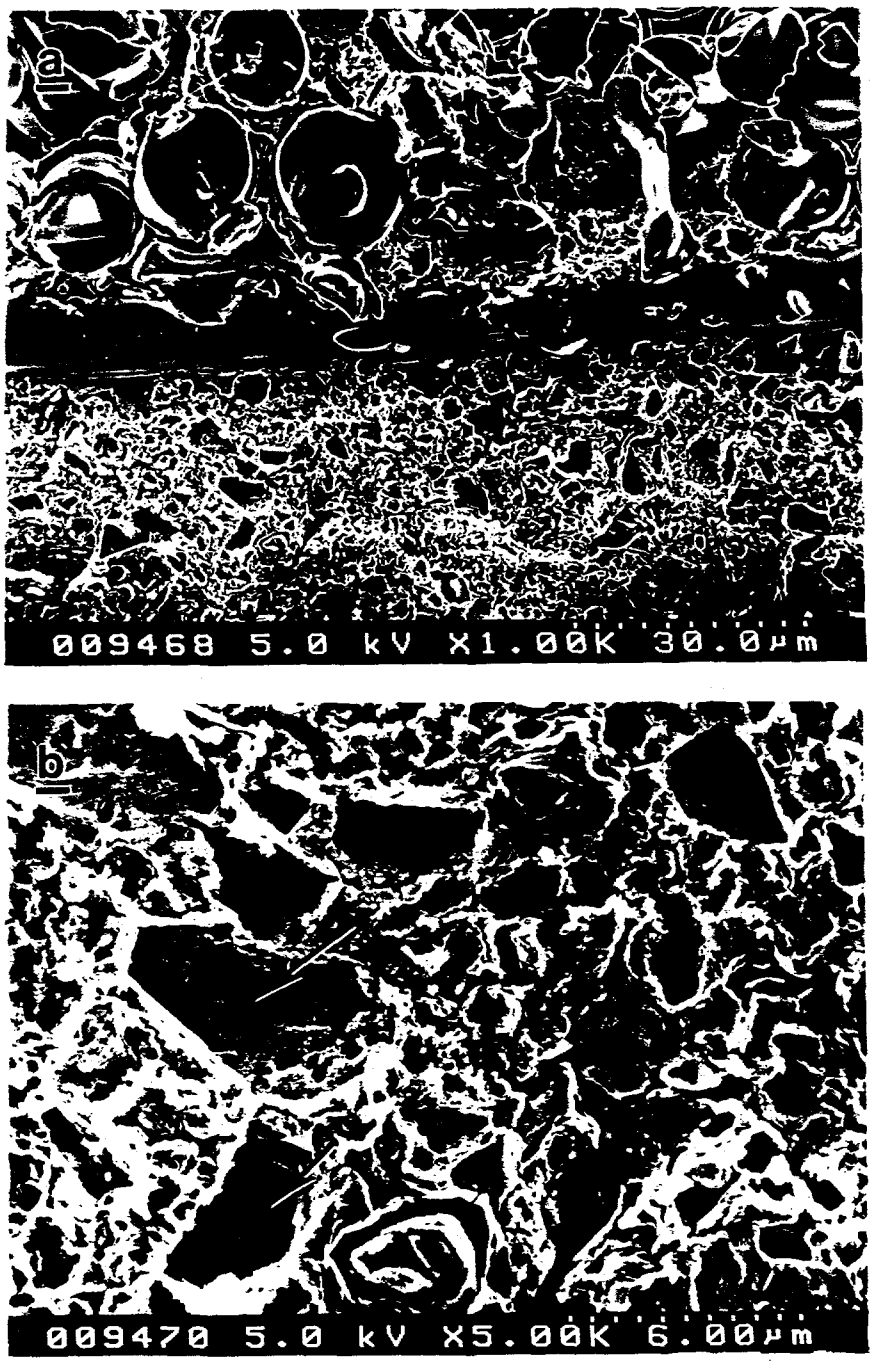

FIG. 7. Fracture surface features of Composite C tested at 950°C. (a) Brittle fracture with substantial formation of boron-containing glass, and (b) Sponge-like graphite observed in fiber bundle associated with particulate-shaped pores due to the oxidation of inhibitors.

ACKNOWLEDGMENTS

The authors thank Drs. P. F. Tortorelli and C. H. Hsueh for reviewing the manuscript. Research sponsored by the U.S. Department of Energy, Assistant Secretary for Energy, Efficiency and Renewable Energy, Office of Industrial Technologies, Energy Efficiency Division and Continuous Fiber Ceramic Composite Program, under contract DE-AC05-84OR21400 with Lockheed Martin Energy Systems, Inc.

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