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Constant load, stressed oxidation testing was performed on T-300 C/SiC composites with a SiC seal coat. Test conditions included temperatures ranging from 350°C to 1500°C at stresses of 69 MPa and 172 MPa (10 and 25 ksi). The coupon subjected to stressed oxidation at 550°C/69 MPa for 25 hours had a room temperature residual strength one-half that of the as-received coupons. The coupon tested at the higher stress and all coupons tested at higher temperatures failed in less than 25 hr. Microstructural analysis of the fracture surfaces, using SEM (scanning electron microscopy), revealed the formation of reduced cross-sectional fibers with pointed tips. Analysis of composite cross-sections show pathways for oxygen ingress. The discussion will focus on fiber/matrix interphase oxidation and debonding as well as the formation and implications of the fiber tip morphology.

INTRODUCTION

Carbon fiber reinforced ceramic matrix composites are proposed for numerous applications where oxidation is a potentially key degradation mechanism. These include turbine structures, combustion chambers, nozzle throats, injector housings, and nozzle extensions in rocket propulsion systems (1,2). In many of the applications, the durations, temperatures, stresses and oxygen partial pressures may be benign enough that C/SiC is the best material of choice. And in cases where the operating environment is too oxidizing, a number of efforts are underway to enhance the oxidation resistance through materials processing or by modifying the design and operating variables. In any case, the key to the exploitation of C/SiC is a knowledge of the time-temperature-stress relationships that dictate life.

The objective of this paper is to set a baseline for the performance of C/SiC composites under stress in an oxidizing environment. The efforts by researchers and vendors to improve the oxidation resistance of these materials are not discussed herein.

TEST MATERIAL AND PROCEDURE

The tensile bars are 152 mm (6 inch), dog bone shaped composite coupons, consisting of plain woven, T300 carbon fibers in a silicon carbide matrix* . The gage sections are 28 mm in length. The fiber bundles consist of 1k tows. The architectural preform is a 0°/90° weave (plain woven). The carbon fibers were coated with a chemically vapor deposited (CVD) pyrocarbon interphase. The silicon carbide matrix was applied into the fiber preform through chemical vapor infiltration (CVI). A seal coating of silicon carbide was applied to the exterior of the composite through CVD. It should be noted that the material comes with a pre-cracked matrix due to the coefficient of thermal expansion mismatch between the carbon fibers and silicon carbide matrix upon cooling from the processing temperature. The density of the coupons on average was 2.06 gm/cc.

Coupons were tested under two different stresses: 69 MPa and 172 MPa (10 ksi and 25 ksi), and at several temperatures: 350°C, 550°C, 750°C, 1000°C, 1250°C, 1400°C and 1500°C. The test coupons were placed in an Instron 8500 Servo-Hydraulic test rig with hydraulic, water-cooled, wedge grips. A MTS 13 mm gage length 300 gram side loaded extensometer was positioned next to the coupon to monitor the strain. Two type R thermocouples measured temperature. The guage section of the test coupons were elevated to the test temperature through the use of an inductively heated SiC susceptor positioned circumferentially around the guage section. Once the coupons were at temperature, the load was applied and maintained. The coupon was exposed to the test environment (i.e., air or argon) throughout the test. Data was acquired through the use of personal computers and in-house developed data acquisition programs. Strain, load, temperature, and time were monitored and recorded throughout the test.

Stressed oxidation testing was conducted until the coupon failed or until 25 hr. had elapsed. Those samples that did not fail after 25 hours were cooled to room temperature and subsequently tested in fast-fracture to measure their residual strength. Two as-received coupons were fast-fractured at room temperature to compare the ultimate tensile strength of the as-received coupons to the residual strength of the coupons that survived 25 hours in stressed oxidation.

RESULTS

The times and strains to failure are shown in Table I. The residual strengths of surviving samples and the strengths of as-received samples are also shown in the table. Samples tested at 350°C/69 MPa and 172 MPa survived 25 hours of stressed oxidation. These samples had residual strengths comparable to the ultimate tensile strength of the as-received coupons. However, the surviving sample, initially tested at 550°C/69 MPa, had a residual strength roughly one-half the as-received strength. This result and the failure of the sample tested at 550°C/172 MPa, suggest that degradation due to oxidation of the carbon fibers is significant at temperatures as low as 550°C. Work by other researchers also found a reduced fracture resistance of C/SiC composites exposed to temperatures as low as 600°C (3).

Samples tested at 550°C/172 MPa and all samples tested at higher temperatures failed within 25 hr. Samples that failed at applied stresses of 69 MPa, had strains to failure that increased as the temperature increased. Samples that failed at stresses of 172 MPa, had a slightly irregular pattern in their strain to failures.

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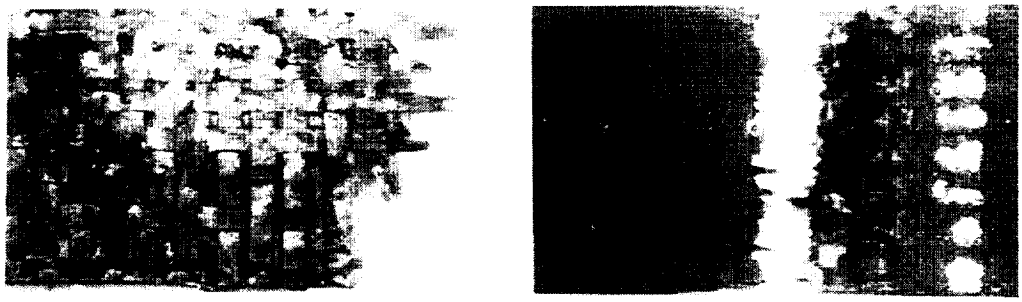
* DuPont-Lanxide Composites, Inc., Neward, DE

Typical fracture surfaces of an as-received sample that was fast fractured at room temperature and a sample that failed during stressed oxidation are shown in Figure 1. The fast fractured samples had a much greater region across which fracture occurred. The fiber bundles separated from the matrix so that only fibers were carrying the load. The fibers appear to fail as a bundle (bundle pull-out) rather than by individual fiber pull-out. As the test temperature increased from room temperature to 750°C, the width across which overall fracture occurred decreased, from 38 mm to 3 mm, and individual fiber pull-out was observed. All samples tested at 750°C and above had similar, narrow fracture widths suggesting that the amount of oxidation across a given cross section is significant enough to cause the material to fail more cleanly and in a less reinforced manner.

Test Temp.	Test Stress	Time to Failure	Strain to Failure	Residual Strength	As-received UTS
°C	MPa		%	MPa	MPa
1500	172	17 min.	1.00		
1500	69	65 min.	0.930		
1400	172	28 min.	0.914		
1400	69	86 min.	0.757		
1250	172	36 min.	0.944		
1250	69	142 min.	0.450		
1000	172	22 min.	0.359		
1000	69	124 min.	0.324		
750	172	22 min.	0.363		
750	69	91 min.	0.209		
550	172	25 hr.	0.450		
550	69	25+ hr.		192	
350	172	25+ hr.		403	
350	69	25+ hr.		383	
					351
					405

Table 1. Test matrix and data for stressed oxidation and fast fracture tests.



(a) (b)

Figure 1. Fracture surfaces of tested material. Left surface of a fast-fracture coupon showing the wide region across which fracture occurred (a). Fracture surface of stressed oxidation sample (750°C/172 MPa) showing a narrower region of failure with individual fiber pull-out (b).

Strain versus time curves for the two stresses are shown in Fig. 2 for the samples tested at 750°C and above. In these plots, three regions were observed that are similar to the trends observed in a typical creep test. After the elastic strain due to loading, the first trend is observed as a inelastic region of decreasing strain rate. The second trend is a steady-state region where the increase in non-elastic strain is very gradual. Although, creep of carbon fibers has been observed (4,5), it is believed that in this region most of the strain is due to an inelastic strain other than creep (this statement will be further supported in the discussion of testing in an inert environment). As the interphase and fibers begin to oxidize, the fibers and matrix debond which accounts for the gradual increase in strain. Also, the woven fiber bundles begin to shift along adjacent void space and straighten along the loading axis. In the third region, there is a sharp increase in strain. In this region, the fibers located in areas of high oxygen concentration, i.e., near the composite edge or along matrix microcracks, have begun to oxidize through their cross-sectional areas. Reduced cross-sectional area fibers begin to fail and no longer bridge cracks. Loads are redistributed and fibers fail progressively until the coupon ultimately fails. The coupons that failed during stressed oxidation showed all three regions while those that survived 25 hr. showed only the first two. Note that on the plot, it is difficult to see all three trends on the short-lived tests due the scaling on the time axis.

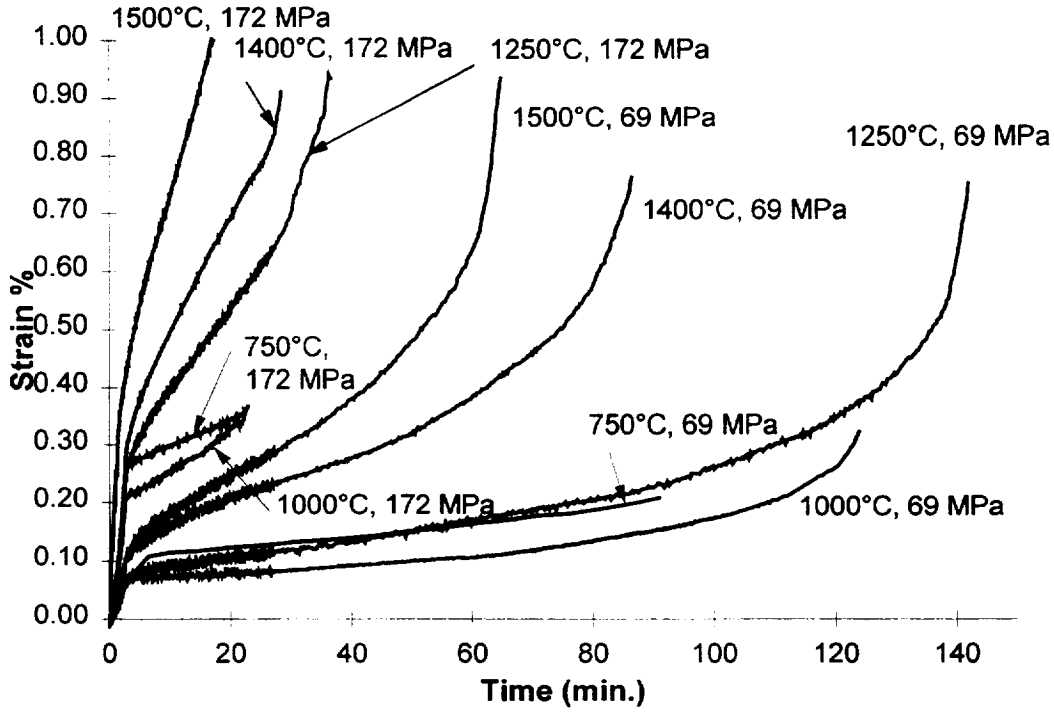


Figure 2. Strain versus time curves for all coupons tested at temperatures of 750°C and above. All specimens failed within 2 1/2 hours and showed the three regions of inelastic strain.

DISCUSSION

The results of stressed oxidation testing do not show a temperature range in which there is a silica self healing process as noted in non-stressed testing. In non-loaded conditions, at temperatures above 1100°C-1200°C the formation of a silica layer has been observed (6,7). At temperatures close to the processing temperature, the matrix cracks begin to close. Also, oxygen reacts with SiC to form a silica layer that further closes the cracks in the SiC seal coating. This sealing effect greatly reduces the amount of oxygen diffusing into the matrix and therefor limits the carbon reactions. The combined results of experimental testing in loaded and non-loaded conditions suggests the applications under which this material may be used. At temperatures in excess of 1100°C, this material could possibly be used in a non-stressed oxygen environment. However, if the material is to be exposed to sufficient stresses in an oxygen environment, the application temperatures must be much lower.

In addition to the air exposures, samples were also tested at 750°C/ 69 and 172 MPa in an inert, argon environment in order to determine the effect of the oxidizing environment on the material. Tests were conducted for a duration of 25 hr. Once the sample was brought to load, there was virtually no increase in strain over the twenty-five hour period. The time versus strain data for the first 5 hr. is shown in Figure 3 along with the data for the samples tested in air. The absence of second and third stage in-elastic strain in the inert tests suggest the strains observed in the tests conducted in air are due to oxidation effects. The reduced lives in air are similar to the results of Holmes and Wu (8), who observed an order of magnitude reduction in sample life at 1400°C, when the oxygen level increased from 1 to 10 ppm.

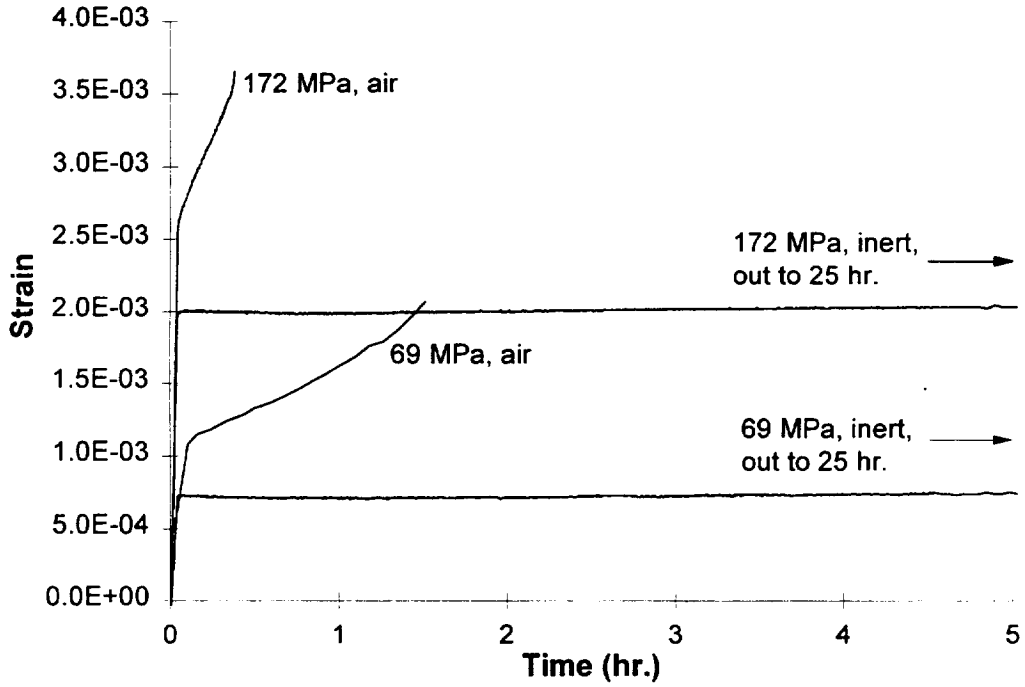


Figure 3. Strain versus time for sustained temperature and load testing conducted in air and argon environments at 750°C/ 69 MPa and 172 MPa.

Cross-sections were cut and polished from the gauge sections of samples that failed during stressed oxidation. Carbon/oxygen reactions were observed in areas of high oxygen concentration such as along sample edges and along cracks. At lower temperatures, 550°C-750°C, the amount of oxidation was much less pronounced when compared to the higher temperature results. The trends at the higher temperatures are illustrated Figure 4. The oxidation process occurred preferentially at the edges and along microcracks. Oxygen was able to diffuse into the matrix along microcracks. Fibers adjacent to the microcracks were consumed by the available oxygen. In some samples, the oxidation process continued to advance to fibers further from the crack until eventually much of the fiber tow had been consumed.

Although some oxidation may occur during cool-down after fracture, most of the oxidation is believed to occur during the stressed oxidation conditions. The reaction rate is an exponential function of temperature. Therefore, as the sample cools, the rate of carbon fiber oxidation becomes much slower. Furthermore, if oxidation was a post-test effect, fiber recession and pointed tip formation would be observed uniformly throughtout the exposed fracture surface. Uniform oxidation patterns were not observed. Pointed fiber tips and receded fibers were observed only in certain areas such as along microcracks, on some fractures edges and in certain tows. Most fibers were blunt suggesting failure due to overload as oxidized fibers transferred their load to non-oxidized fibers. Analysis of cross-sectional areas show that during the test, oxygen was able to diffuse through cracks in the external SiC coating and react with fibers in the interior of the matrix rather than oxidation occurring only after failure on exposed surfaces.

Figure 4. Optical photograph of C/SiC cross-section of a sample stressed oxidation tested at 1000°C/ 172 MPa.

Figure 5. SEM micrograph of the fracture surface of a sample tested at 550°C/ 172 MPa.

Pointed fiber tips and receded carbon fibers were observed in all samples that failed during stressed oxidation. The formation of pointed fiber tips is an oxidation effect and has been observed by other researchers (9,10). The pointed carbon fiber tips form due to oxygen attacking from the side of the fiber as shown in Figure 5. The early stages of the oxidation process begins at the pyrocarbon interphase. Once the fiber is exposed, it begins to narrow as its cross-sectional area is reduced due to oxidation. Pointed tips form as oxidation continues through the cross-sections of the fibers. The density of the carbon fibers may also contribute to the formation of pointed tips. Lamouroux, et al have reported that the inner core of carbon fibers is more dense so

that the oxidation rate is slower in the interior of the fibers due to less surface area being available for oxidation (11).

The overall effect oxidation can have on the composite is illustrated in Figure 6. A crack is observed to traverse vertically through the material. Fibers that once bridged the crack have oxidized through their cross-sections and have formed pointed fiber tips. As oxidation continues, the carbon fibers continue to recede from the crack. These non-bridging fibers weaken that region of the composite and cause loads to be redistributed. As sufficient loads are reached, the material will fail along non-bridged cracks and along cracks bridged by fibers of reduced cross-sectional areas as shown in Figure 7.

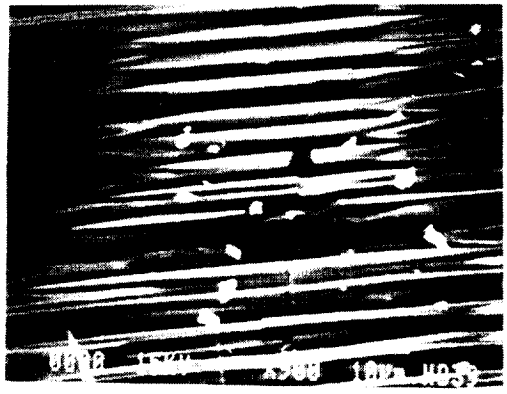


Figure 6. SEM micrograph of the fracture surface of a sample tested at 1000°C/ 172 MPa.

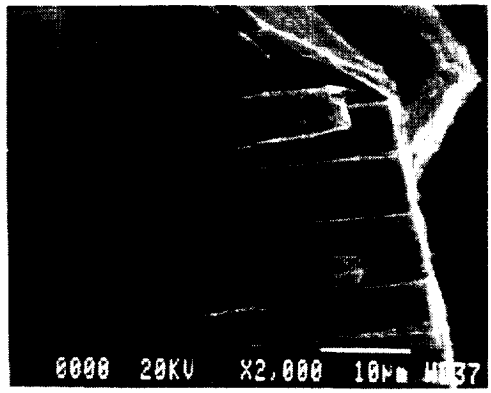


Figure 7. SEM micrograph of the fracture surface of a sample tested at 750°C/ 172 MPa.

CONCLUSIONS

The presence of an oxidizing environment dramatically affects the performance and mechanical properties of unprotected C/SiC composites. Materials exposed to stressed oxidation conditions had reduced strengths and reduced lives due to oxidation of the pyrocarbon interphase and the carbon fibers. Diffusion of oxygen occurred through cracks in the SiC external seal coating and continued into the matrix along microcrack pathways. Composite failure occurred through the propagation of microcracks. Strain to failure is dependent on the test temperature and was observed to increase with temperature. The life of the material is dependent on the test temperature and stress. In general, as the temperature and stress increase, the life of the material decreases. However, temperature had less of an effect at 750°C and higher. In order to reduce the susceptibility of C/SiC to oxidation, enhanced or protective systems must be investigated.

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