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Environmental embrittlement of SiC_f/SiC composites

N.S. Stoloff*, P. Lipetzky[1], G.J. Dvorak

Materials Science and Engineering Department, Rensselaer Polytechnic Institute, 110 8th Street, Troy, NY 12180-3590, USA

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Abstract

The effects of surface condition, moisture and temperature on the mechanical behavior of SiC_f/SiC composites produced by Dupont Lanxide are described. Elastic moduli and tensile strengths have been established at temperatures between 25 and 1200°C. A degradation in properties is noted by thermal exposure alone, but the effect is altered by the presence of moisture in the test atmosphere. The influence of a surface coating on the observed behavior is described. Changes in microstructure accompanying environmental embrittlement are described. Implications for structural applications of these composites are discussed.

Keywords: Environmental embrittlement; SiC/SiC composites

1. Introduction

Silicon carbide fiber-reinforced composites have been examined for heat management and structural applications. Environments to which these composites may be exposed may be oxidizing or reducing and may contain water vapor, hydrocarbons and oxides. It has become apparent that these environments may have serious adverse effects on mechanical behavior, and that these effects may differ with microstructural variables and applied coatings. Short term mechanical behavior will be affected by fiber and matrix strength, interfacial strength, fiber architecture and porosity. It has been shown that the ultimate strength and fracture resistance of a SiC_f/SiC composite increase with increasing fiber coating thickness, reaching a maximum for a thickness near 0.3 μm [1]. A strong correlation between interfacial strength and composite strength has been noted by Gomina et al. [2]. High temperature soaking in argon prior to mechanical testing drastically reduces tensile strength and fracture energy while causing considerably less fiber pull-out. A previous study in our laboratory has shown that water vapor can be a stronger SiC oxidant than pure oxygen [3]. The atmosphere also affects the morphology of the silica layer, and this is reflected in the mechanical properties.

This investigation focuses on the effects of moist and dry air on the high temperature lives of SiC_f/SiC composites produced by Dupont Lanxide Inc. Effects due to surface coatings and cyclic deformation will also be described.

2. Materials

The microstructure of the SiC_f/SiC composites used in this study is shown in Fig. 1. The material consists of a plain weave [0/90] fabric, utilizing Nicalon fibers, which is chemically vapor infiltrated subsequently with oxidation inhibitors and then with crystalline SiC. Properties of the fibers and the composite are listed in Table 1 [4]. Approximately 10 such plies are consolidated into the final plate. Tensile samples were machined in the 0° direction and completely seal coated with additional SiC. Following consolidation and densification, tensile samples were cut from the large sheet. Machining removed the coating from sample edges; therefore, some specimens were recoated so as to determine whether edge effects were important during subsequent testing.

* Corresponding author. Tel.: +1-518-276-6436; fax: +1-518-276-8554.

E-mail address: stolon@rpi.edu (N.S. Stoloff)

[1] Now at Pittsburgh Materials Technology Inc., Large, PA 15025, USA.

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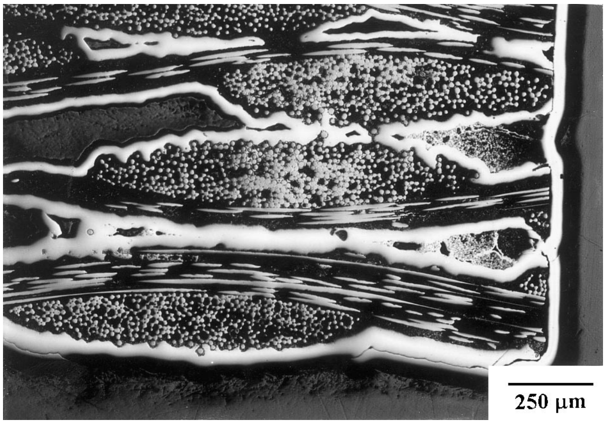

Fig. 1. Cross-section of SiC/SiC composite, showing fiber bundles.

Table 1
Room temperature properties of SiC/SiC composite and Nicalon fibers[a,b]

Composite stiffness, E	138 GPa
Composite thermal conductivity, λ	6.9 $Wm^{-1} K^{-1}$
Composite strength, σ_{ult}	230 MPa
Composite elongation, ε_{fail}	0.4%
Composite proportional limit, σ_{PL}	55 MPa
Composite heat capacity	820 J $kg^{-1} K^{-1}$
Composite density, ρ	2.35 gcm^{-3}
Residual porosity	10%
Interlaminar shear strength, τ_{ult}	31 MPa
Nicalon stiffness, E	220 GPa
Nicalon diameter	14 μm
Nicalon volume fraction, V_f	40%
Nicalon elongation, ε_{fail}	1.4%
Nicalon expansion coefficient, x	3.2×10^{-6} K^{-1}

[a] DuPont Lanxide Inc., 1300 Marrows Road, Newark, DE 19714-6077, USA.
[b] Data provided by the manufacturer.

3. Experimental procedures

Several mechanical test procedures were used. Tensile tests were run in stress control on a MTS servo-hydraulic system. Specimens had a reduced gauge section of 0.25×0.8×7.5 cm, with a total length of 20 cm. Specimens were gripped by manual face-loaded blocks on aluminum tabs cemented to the specimen ends. An alignment jig consisting of a precision-ground flat steel strip with eight resistance strain gages was used in order to insure proper alignment as well as uniform distribution of the tensile load. Strain was measured directly from the gage length using an MTS high temperature extensometer. All tensile tests were carried out in laboratory air at temperatures to 1200°C. In addition, static tests to determine the effects of stress and environmental exposure on lifetime were carried out in dry and wet air. Static tests at 1000°C were carried out to rupture or to run-out at 240 h. A 6 h run-out limit was used to investigate the temperature dependence of life. These tests were performed by holding a fixed stress at a given temperature either for 6 h or to rupture. If the sample survived these conditions, temperature was increased by 50°C and testing was continued to run-out or rupture. Young's modulus was measured periodically by slightly altering the stress and measuring the change in strain in order to measure the evolution of damage. Recovery of damage was induced by thermally soaking samples under stress-free conditions, following an initial load cycle to 120 MPa. Moist air was produced by bubbling air (0.1 l/min at RTP) through a reservoir of water held at 90°C into an atmosphere containment jacket around the sample.

Cyclic tests were run at a standard frequency of 10 Hz and stress ratio of 0.1, although these parameters were varied between 5 and 50 Hz and $R=0.1$–0.5, respectively. Fatigue run-out was defined as survival for 10^6 cycles. Following run-out at any given stress the maximum stress was raised in 10 MPa increments, with cycling continuing to run-out or failure.

4. Experimental results and discussion

The tensile stress–strain behavior is plotted in Fig. 2 for room temperature and three elevated temperatures. There does not appear to be a strong temperature dependence of stiffness, proportional limit or damage–regime slope. The tensile strength is highest at 1200°C, in contrast to the fiber strength, which drops sharply above 1000°C [5]. Table 2 summarizes the properties measured in this study.

No noticeable fiber degradation was observed for any stress applied at temperatures below 1000°C. Fiber pull-out and porosity as well as an intact fiber-bundle coating were observed at all temperatures to 1000°C, but at 1200°C the amount of pull-out was sharply reduced, thereby implying that the strength of the fiber–matrix interface had increased above 1000°C. Also, samples tested at 1200°C displayed a much higher matrix crack density. Specimens loaded to stresses that did not cause failure showed that significant transverse cracking begins at the proportional limit.

The results of delayed failure tests are shown in Fig. 3. There is no apparent run-out stress in dry air between 30 and 150 MPa; instead there is a linear relation between the logarithm of rupture time and the applied stress. Similar experiments carried out in moist air gave equivalent results. However, initial data suggest that moisture in air may improve life at stresses below 70 MPa.

Composite damage was monitored by measurement of specimen modulus. The evolution of modulus for a stress level of 80 MPa at 1000°C is shown in Fig. 4. There is a steady decrease in modulus prior to failure

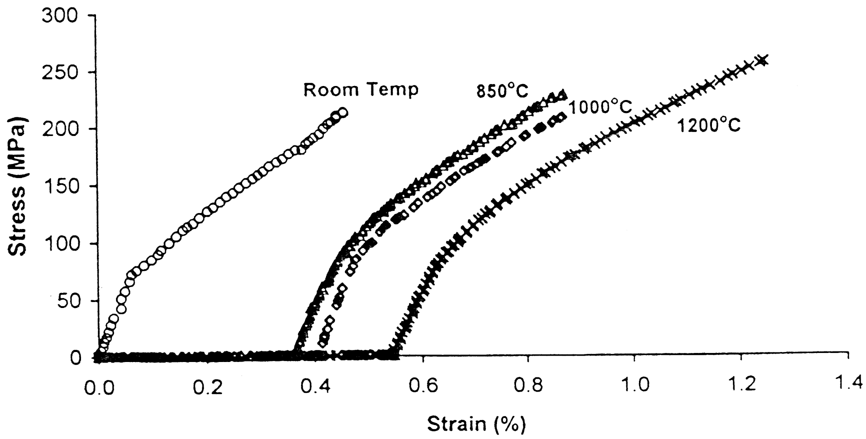

Fig. 2. Tensile curves as a function of temperature.

Table 2
Tensile properties as a function of temperature for SiC/SiC

Property	Room temperature	850°C	1000°C	1200°C
E (GPa)	119.95	112.4	111.8	100.7
σ_{PL} (MPa)	67.7	84.1	77	76
σ_{ult} (MPa)	211.5	228.0	206	258
τ_{ult} (MPa)	23.5	–	–	–
ε_{fail}^{tot} (%)	0.458	0.865	0.858	1.248
ε_{therm} (%)	0.0	0.356	0.420	0.542

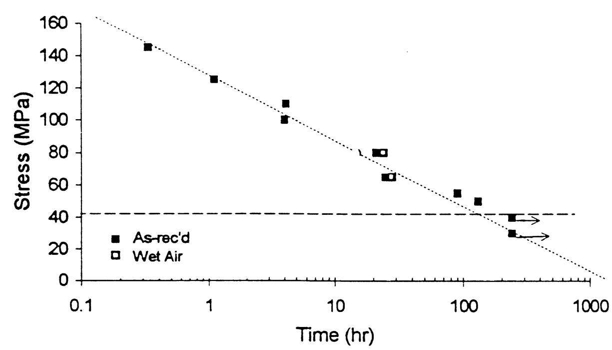

Fig. 3. Static fatigue lifetimes, 1000°C.

for tests in dry air, but moisture in air causes a high retained stiffness. At stresses above 90 MPa no dependence of modulus on moisture was noted. However, for stresses below 60 MPa the composite displayed an incubation period prior to the onset of a decay in modulus. This phenomenon has previously been attributed to the relative rates of silica formation, silica density and adherence [3,6]. At 1200°C the Nicalon fibers lose both stiffness and strength.

Additional stress rupture tests were run at increasing temperatures. Six hour survival temperatures at 100, 130 and 160 MPa are listed for both dry and wet air in Table 3. Note the small degree of loss of temperature capability in wet air. Survival temperatures are reduced by about 50°C when 25% of the seal coat is removed. Fig. 4 also shows that composite life at 1000°C is reduced significantly when part of the coating is removed, independent of the moisture content of the air.

Damage recovery capability was also studied. Fig. 5 displays modulus data following prestrain damage and stress-free exposure to dry and wet air. The composite exhibited extensive recovery of the modulus in both environments after only 10 h of exposure, with water vapor causing recovery to nearly 100% of the original modulus. Longer exposure times had no additional effect. It has been suggested that recovery comes about due to the formation of SiO_2 on SiC crack faces [3]. Oxygen peaks were observed by energy dispersive analysis on post-recovery matrix crack surfaces, but not on samples that were not subjected to the recovery treatment. The extent of recovery is such that recovered samples subjected to static fatigue showed lifetimes similar to those of undamaged samples.

Thermally soaking as-received samples for 1 week at 1200°C in air or in argon substantially reduced both the ultimate strength (50%) and stiffness (10%). Thermal cycling between 20 and 1000°C resulted in no loss of strength or stiffness for up to 50 cycles.

Fig. 6 shows the high cycle fatigue behavior, recorded as stress maxima vs total number of load cycles. Samples consistently reached run-out at 23°C [Fig. 6(a)], for stress maxima below about 85% of the ultimate tensile strength (UTS) of 180 MPa, independent of surface coating, atmosphere, load ratio or test frequency. Higher stress maxima caused a sharp drop in the cycles to failure. At 850, 1000 and 1200°C, on the other hand, the endurance limits were less than 30% of the UTS, see Figs. 6(b), (c) and (d). Varying load ratio and frequency

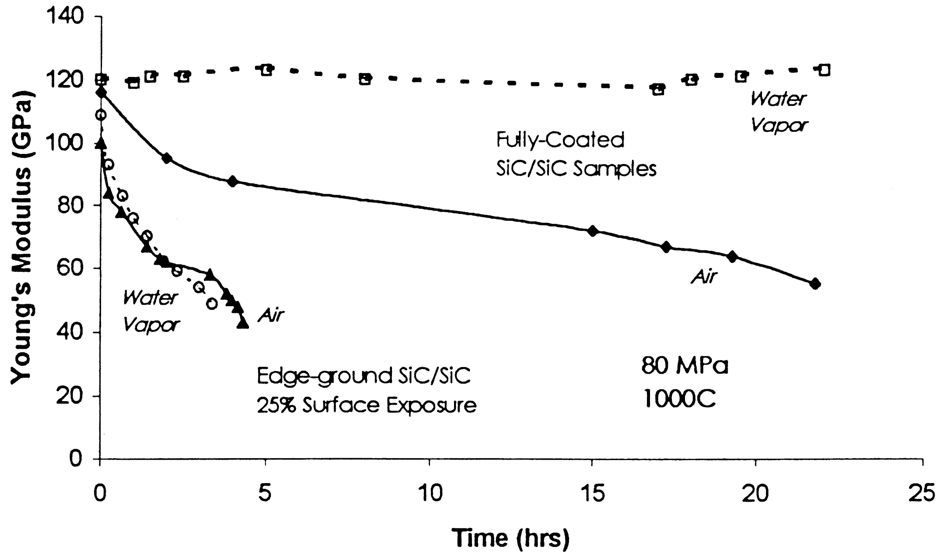

Fig. 4. Modulus retention at 1000°C.

Table 3
Stress, temperature, creep rupture behavior

6-h Survival stress (MPa)	SiC/SiC		
	Dry air (°C)	Wet air (°C)	Uncoated (°C)
100	1000	1000	900
130	750	700	700
160	700	650	650

had no significant effect on the results. Fig. 6(c) shows that the integrity of the surface coating becomes critical at 1000°C. In the event of a 25% coating loss, the endurance limit drops from 80 to 55 MPa, apparently due to chemical attack of the uncoated edges during the test. The endurance limit at 1200°C [Fig. 6(d)], is also near 80 MPa, in close agreement with the proportional limit and the onset of matrix cracking.

A change in Young's modulus has been shown to indicate the damage state in this material. Measurements of modulus during stress cycling are plotted in Fig. 7 for two conditions, air and water vapor. The results show that cycling within a fixed range (8–80 MPa) can cause the modulus to decrease prior to failure. Samples tested in air show a large decrease in modulus, while those tested in water vapor do not. At stresses above the endurance limit atmosphere plays no role and samples fail within a short period, consistent with Fig. 6(c).

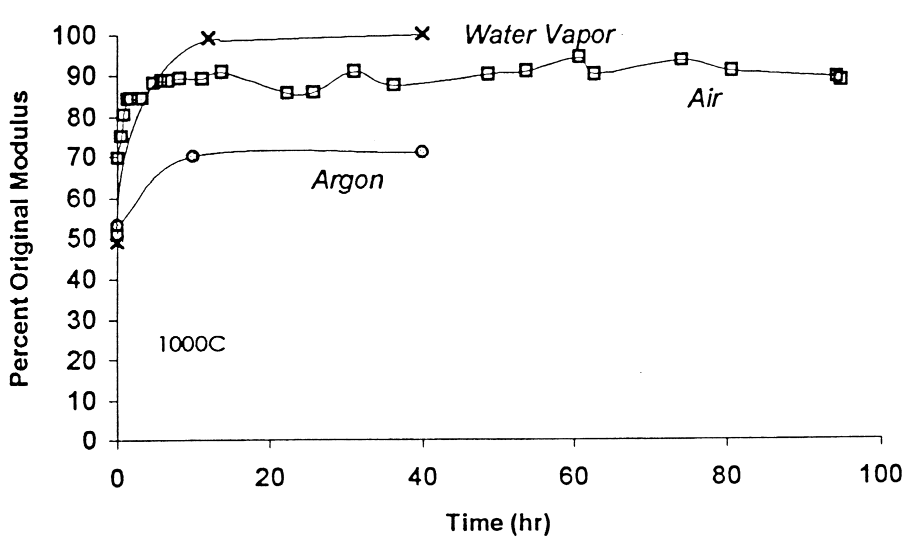

Fig. 5. Modulus recovery data for exposure at 1000°C.

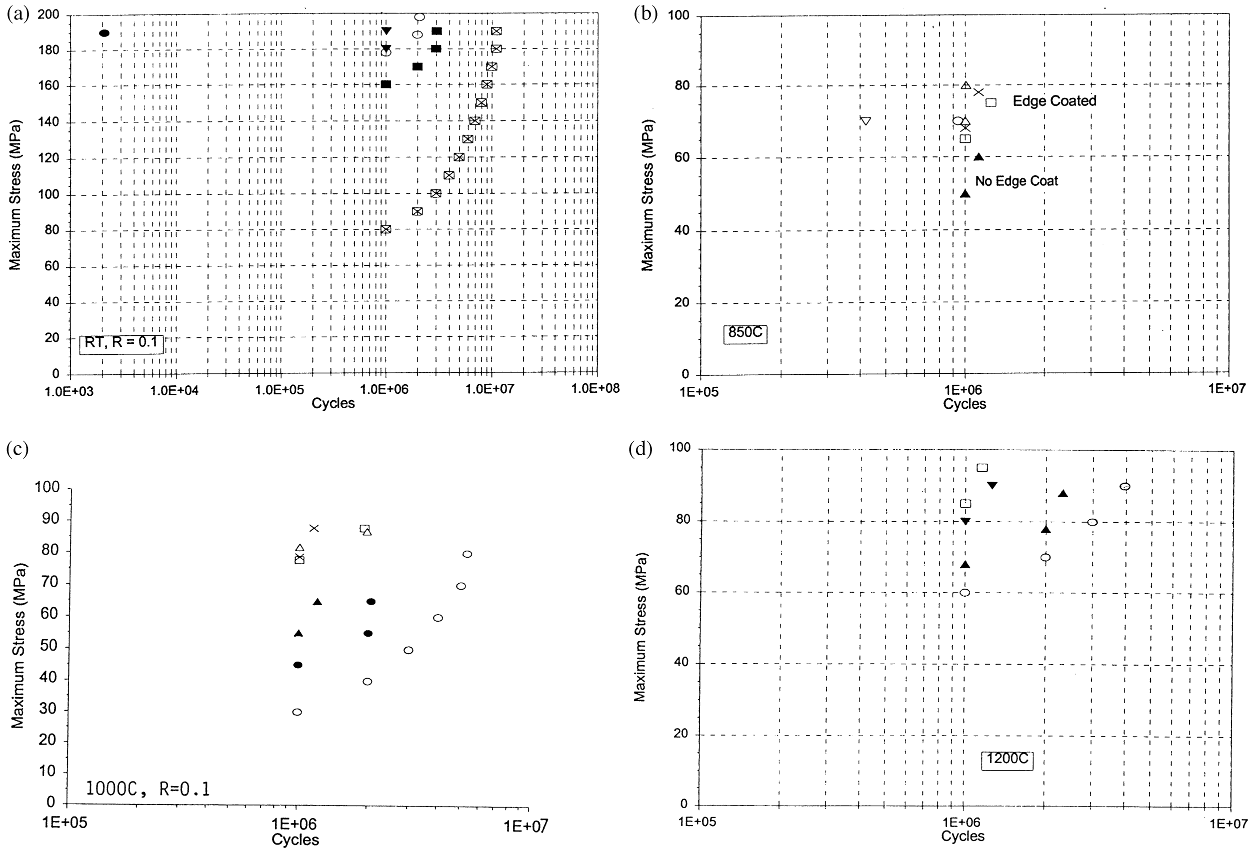

Fig. 6. High cycle fatigue endurance data. Each symbol type corresponds to one sample. If 10^6 cycles were survived, stress was raised and cycling continued. Last point on each curve represents failure. (a) Tested at room temperature. Samples reached run-out (10^6 cycles) for all stresses below 180 MPa. All samples fully coated. (b) Tests at 850°C. Run-out was reached for stress maxima less than approximately 60 MPa for coated samples. One edge-ground sample, ▲, was tested and reached run-out at maximum stress of 50 MPa. (c) Tests at 1000°C. Load ratio and frequency did not play significant roles ($R=0.1$–0.5, $\nu=5$–50 Hz). Solid symbols are for edge-ground samples. (d) Tests at 1200°C reveal an endurance limit of ~75 MPa. These samples were all fully coated, $R=0.1$, 10 Hz. All samples are coated.

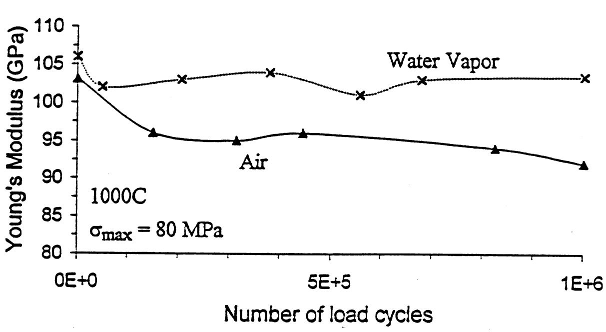

Fig. 7. Modulus retention during cyclic loading at 1000°C.

5. Summary and conclusions

SEM and optical analyses revealed the presence of Nicalon fiber bundles woven into 0–90 plies, which are overlaid to form the bulk composite. The bundles consist of coated Nicalon fibers and a significant amount of filler material, all surrounded by a SiC bundle coating. An additional SiC coating is applied to the sample surface to inhibit environmental attack at elevated temperatures. Tensile experiments revealed little change in stiffness at temperatures to 1200°C for a stress-controlled loading rate of the order of 1 MPa s^{-1}. The proportional limit was established as the stress at which matrix cracking began. Fiber-matrix bond strength and composite strength peaked at 1200°C. Moisture content in air did not affect short-term behavior at any temperature, but there was an effect in long term tests. Static fatigue life for the composite at 1000°C obeys a linear relationship between stress and log of rupture time up to 240 h exposure over a stress range of 30–150 MPa. Data suggest that moist air may promote long term life by forming a dense, coherent silica layer that can both support load and retard oxygen ingress. Removal of 25% of the seal coating can reduce specimen life by up to 80%. The 6 h survival temperature is affected by stress, loss of surface coating and exposure to water vapor. Water vapor also causes the composite to retain or regain a high modulus under load, and causes recovery to nearly 100% of the original stiffness if recovery is performed at stresses near zero. This is probably due to the formation of silica on matching crack faces. Exposure to dry air causes less modulus retention and less modulus recovery. Cyclic experiments confirm the importance of retaining all of the surface coating to achieve maximum life at 1000°C. Modulus changes are a useful measure of composite damage or recovery under both cyclic and static loading.

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