

ENVIRONMENTAL AGING DEGRADATION IN CONTINUOUS FIBER CERAMIC COMPOSITES

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ABSTRACT

The thermal stability of two continuous fiber ceramic composites (CFCC's) has been assessed. A Nicalon/CaO-Al₂O₃-SiO₂ (CAS) glass-ceramic matrix composite has been subjected to unstressed, oxidation heat-treatments between 375 and 1200°C, after which the material was tested in flexure at room temperature. The static fatigue behavior of a chemical vapor infiltrated (CVI) Nicalon/SiC ceramic matrix composite has been assessed in air, between 425 and 1150°C, both with and without a protective seal coating. Severe property degradation was observed due to oxidation of the graphitic fiber/matrix interlayer in both CFCC's.

INTRODUCTION

The mechanical behavior of continuous fiber ceramic composites (CFCC's) is primarily dictated by the nature of the fiber/matrix interface [1,2]. The development of 'weak' interfaces generally results in composite fracture resistance far exceeding that of the matrix alone. Typically these interfaces are carbon based and are either grown *in-situ*, for example in glass-ceramic matrix composites (GCMC's) [3-5], or deposited by chemical vapor deposition (CVD), for ceramic matrix composites (CMC's) such as SiC fiber reinforced SiC [6,7].

The benefits observed with carbon based interfaces are diminished during elevated temperature (>800°C) fast fracture in oxidizing environments, when rapid oxidation of the carbon interlayer can occur [8,9]. Degradation of the interface can also arise during extended duration aging at intermediate temperatures (600-900°C) [10-14], with gradual 'pipeline' oxidation of the interface being responsible in this instance. Under these aging conditions it has been demonstrated that oxidative removal of the carbon interlayer can be followed by the surface oxidation of the fiber to form silica, resulting in a strong fiber/matrix bond [11,12]. Although it is clear that these materials can exhibit severe degradation phenomenon at intermediate temperatures, very little information is available on stability at temperatures below 600°C. The purpose of the present work is to investigate the thermal stability of two CFCC's over a wide temperature range, from 375 to 1200°C, and for extended duration's in loaded and unloaded conditions.

EXPERIMENTAL PROCEDURE

MASTER

The CFCC materials used in the present study were; a cross-ply [0,90]_{3S} Nicalon fiber/CaO-Al₂O₃-SiO₂ (CAS) Type II matrix glass-ceramic composite, which was manufactured by Corning (NY, U.S.A.), and a woven 'forced' chemical vapor infiltrated (FCVI) Nicalon fiber/SiC matrix ceramic composite prepared at Oak Ridge National Laboratory [6,7]. The Nicalon/SiC material was provided in both as-machined and 'seal-coated' conditions, where the 'seal-coating' is a SiC layer applied by CVD. Both Nicalon/SiC variants had a graphitic fiber/matrix interlayer of ~300 nm thickness. The fiber contents of the two materials were ~35 and ~43 volume percent for the Nicalon/CAS and the Nicalon/SiC respectively.

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Aging heat-treatments, without applied load, have been performed in air on Nicalon/CAS test bars (50 x 3.5 x 2.35 mm) at temperatures between 375 and 1200°C, for up to 500 h. The aging heat-treatments were performed by inserting the test bars, sited on Pt foil, into a furnace pre-heated to the aging temperature, with removal from the furnace at temperature, after the test duration was complete (air quench). Flexure testing was performed on as-received and aged Nicalon/CAS samples in three point bend (outer span 40 mm, giving a span to depth ratio of ~17:1), at a cross-head speed of 0.5 mm/min. Acoustic emission was monitored during testing. A minimum of two tests were performed for each aging condition.

The static fatigue behavior (time to failure) of the FCVI Nicalon/SiC composite was assessed in four point bend (α -SiC test fixture, 40 mm outer and 20 mm inner spans) between 425 and 1150°C. Test bars, 3 x 4 x 50 mm, were preloaded (<15 MPa applied outer fiber stress) and then heated to the test temperature. They were subsequently held at temperature for 20 minutes in order to reach thermal equilibrium, prior to application of the desired test stress. The applied stress was then held constant until the test bar failed, at which point a micro-switch interrupts the furnace power, allowing the fractured bar to cool rapidly (~30 minutes to RT).

Microstructural characterization was performed by both scanning and transmission electron microscopy (SEM and TEM respectively). Interface compositional profiles were obtained by scanning Auger microscopy (SAM), with notched bars fractured *in-situ* within the microscope.

RESULTS

The effects of thermal aging on Nicalon/CAS

The matrix phase of the Nicalon/CAS composite used in the present study is devitrified to anorthite ($\text{CaAl}_2\text{Si}_2\text{O}_8$), with a small volume of zircon (ZrSiO_4), present primarily at the fiber/matrix interface. TEM demonstrated the presence of a thin 'carbon-rich' interlayer (~40-50 nm thick) between the fibers and the matrix (Fig. 1a) [14]. This interlayer thickness was consistent for all the interfaces examined in this TEM foil. SAM examination of the as-fabricated Nicalon/CAS composite confirmed the carbon layer thickness, and demonstrated that the interlayer was essentially 'pure' carbon (Fig. 1b). An apparent transition from the 'pure' carbon layer to a consistent fiber composition occurs over the next ~100 nm. Diffusion of the matrix elements, notably Ca, occurs to a depth of several hundred nm into the fiber surface during composite fabrication (Fig. 1b). These observations are generally similar to those made for Nicalon/ $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ (LAS) composites [15].

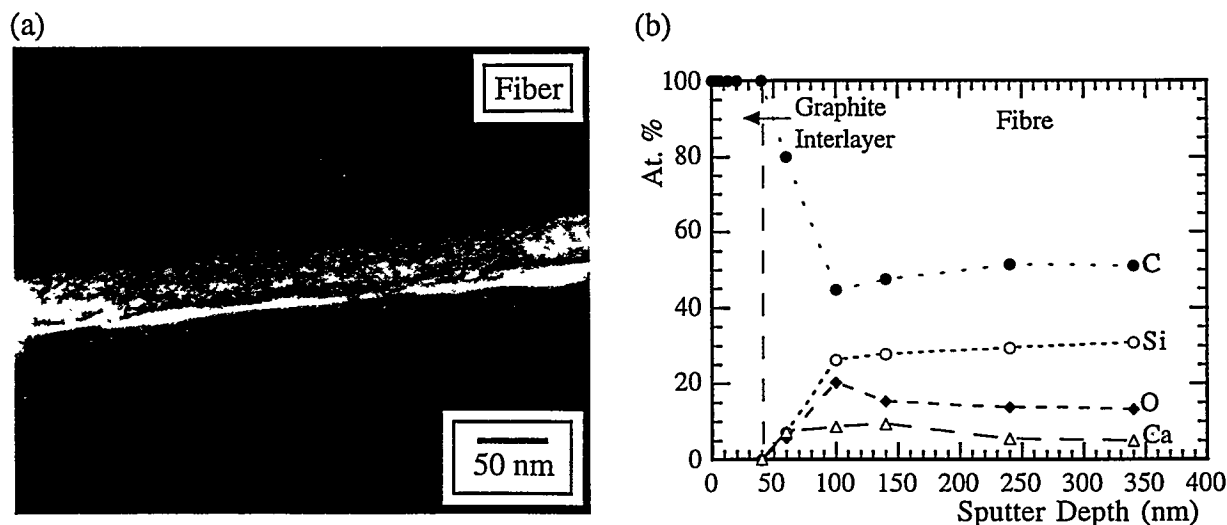


Figure 1. a) Bright-field TEM micrograph of the carbon interfacial layer in the Nicalon/CAS composite. b) SAM profile of the fiber/matrix interface.

The effects of aging heat-treatment temperature (for 100 h) upon the room temperature flexure strength and proportional limit are shown in Figure 2. It is clear that considerable property degradation occurs at aging temperatures as low as 450°C, with a considerable drop in the proportional limit, which closely correlates with the onset of matrix microcracking (determined by acoustic emission). At higher temperatures, 600-800°C, a significant reduction in the flexure strength is noted, however the proportional limit stress is increasing at these temperatures.

Aging in this intermediate temperature range results in a transition to a brittle failure mode, as demonstrated by the load/deflection curves obtained (Fig. 3a). Conversely, when aging at temperatures above 800°C, high strength is retained (Fig. 2), with a 'ductile' composite failure mode (Fig. 3b).

Negligible fiber pull-out is observed on the fracture surfaces of samples aged in the intermediate temperature range (450–800°C), indicating either a strong fiber/matrix bond or increased sliding stress is occurring in comparison to the as-fabricated composite (which exhibits considerable fiber pull-out). These macro-mechanical observations of the change in interface behavior have been confirmed by fiber push-down [14]. It is apparent that the change in pull-out behavior correlates with the transition to a brittle failure mode at the intermediate aging temperatures (Fig. 3a). Samples aged at 1000°C and above exhibited significant fiber pull-out, comparable to the as-received material, although the average pull-out lengths were lower. Examination of samples aged at the higher temperatures (1000°C and above) demonstrates that the fiber ends become 'plugged' with SiO₂, formed by oxidation of the exposed surface fibers, as previously observed in both Nicalon/CAS [11] and Tyranno/BMAS [12].

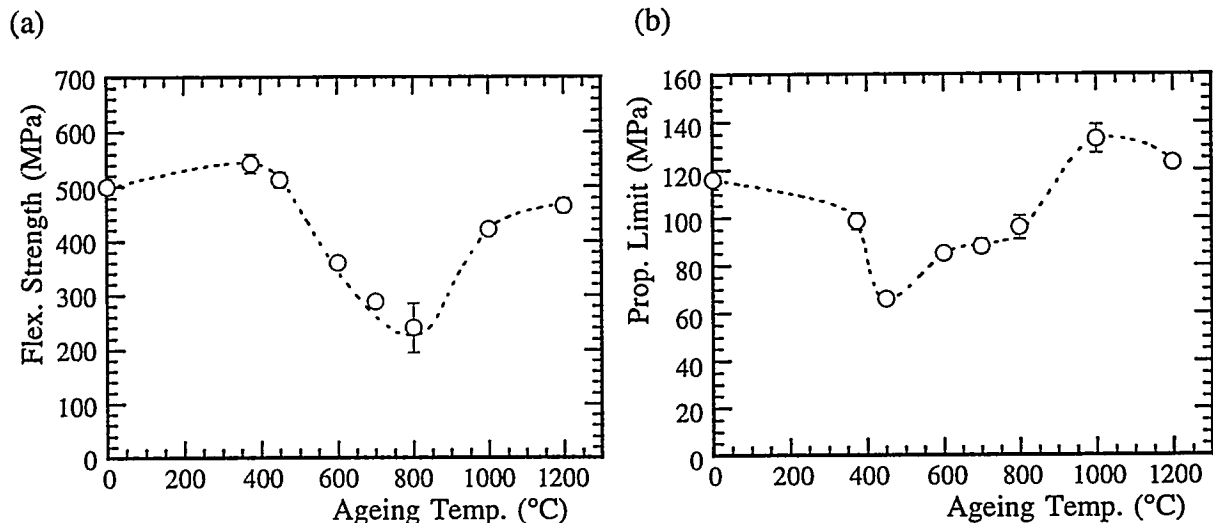


Figure 2. The effects of aging temperature upon a) the room temperature strength and b) the proportional limit.

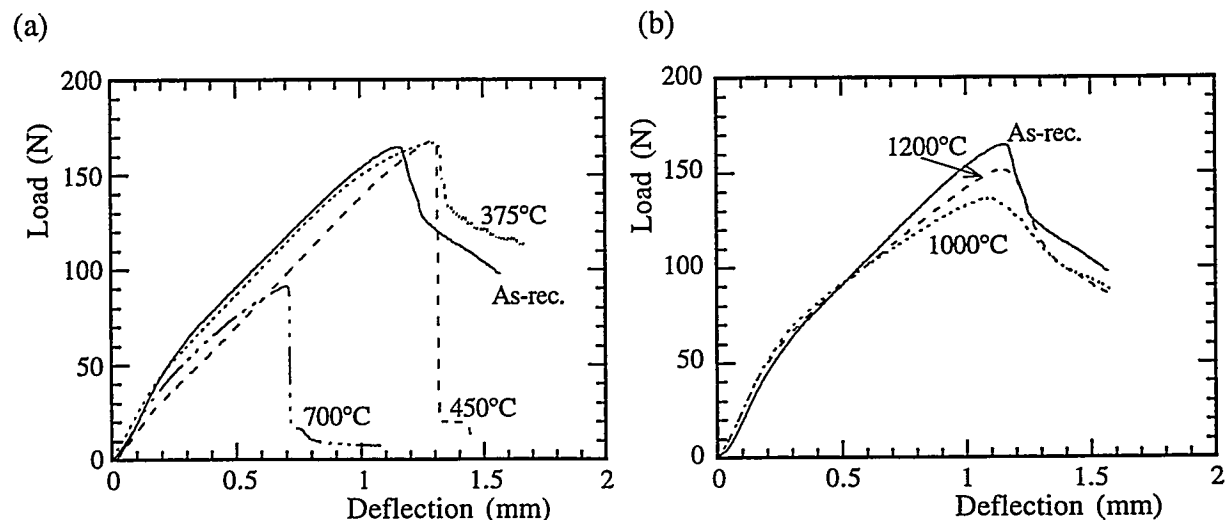


Figure 3. The effects of aging heat-treatment temperature upon the room temperature stress-strain behavior; aging at a) temperatures up to 700°C and b) at 1000°C and above. The stress-strain curves for the as-fabricated material are shown for comparison.

The interfacial microstructure of the thermally aged composites has been assessed by both cross-sectional TEM and SAM, the latter involving fracture of aged test bars *in-situ* in the SAM (to ensure 'clean' fiber/matrix surfaces). SAM profiles of the surface of Nicalon fibers in samples aged at 450 and 700°C are shown in Fig. 4. These profiles are taken approximately 500 μ m from the surface in a central 90° ply of the material. Only minimal carbon is present after aging at 450°C for 100 h (Fig. 4a), compared to the as-received composite (Fig. 1b). It was generally noted, both from TEM and SAM, that debonding occurred at the matrix/carbon interface, such

that the SAM data shown is a profile through the carbon interlayer into the fiber (negligible carbon was detected in the matrix troughs, from which fibers had been pulled-out during fracture in the SAM). A very thin (~10-15 nm) carbon layer remains intact when aging at 700°C for 100 hours, and the fiber surface is more SiO₂ rich than the as-received material (Fig. 4b), as demonstrated by the high surface Si(O) content. Initial TEM examination of the samples aged at 600 and 700°C indicates that nearly complete retention of the carbon interlayer can occur in the center of the test bar. This indicates that the oxidation reaction is either partially blocked or does not proceed rapidly enough for complete removal of the carbon interlayer. It has previously been observed that voids can form at the interface in a similar Nicalon/CAS material when aging at these temperatures [11].

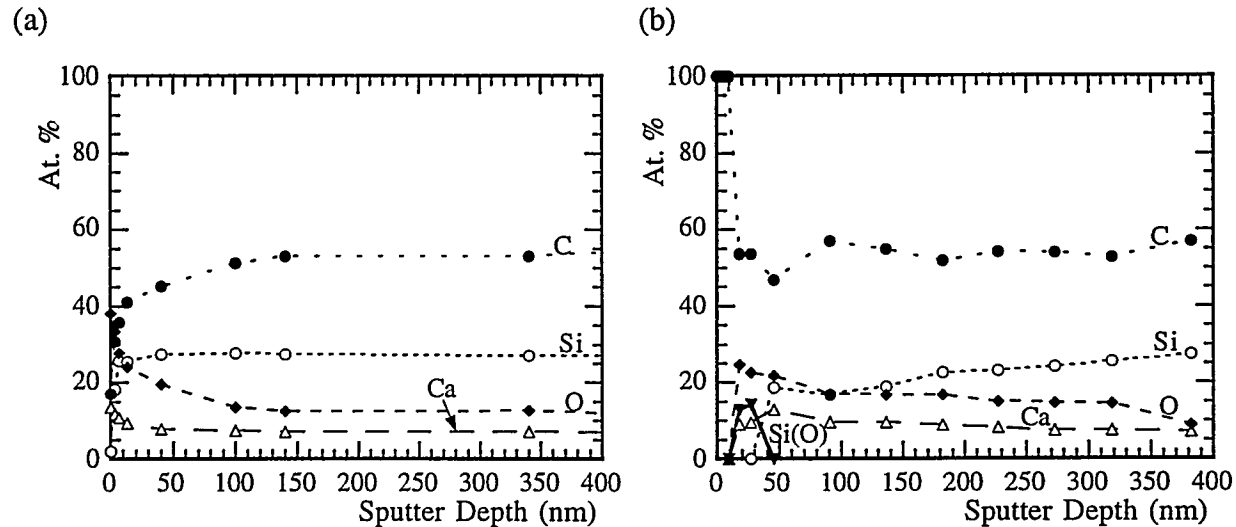


Figure 4. SAM profiles of the interlayer composition after thermal aging at a) 450°C for 100 h, and b) 700°C for 100 h.

Long term (500 h) aging at 1000 to 1200°C does not result in any significant degradation of the room temperature mechanical behavior of the Nicalon/CAS composite (Table I), and 'ductile' composite failure modes are retained, similar to the as-received material. Considerable fiber pull-out is observed to within approximately two fiber diameters of the tensile surface, with pull-out lengths being comparable to the as-fabricated material. It was also apparent from SEM investigation that the anorthite matrix was highly resistant to grain growth, even after an extended duration hold at 1200°C, indicating good high temperature stability.

Table I. Mechanical performance of Nicalon/CAS CFCC's after long term (500 h) aging at temperatures above 1000°C. Bending modulus determined from the first linear portion of the load-deflection trace, pull-out lengths measured from the outer tensile ply only. Data obtained for the as-fabricated material and after aging at 700°C for 100 h is shown for comparison.

Aging Condition	Flexure Strength (MPa)	Percent Strength Retention	Prop. Limit (MPa)	Bending Modulus (GPa)	Average Pull-out Length (μm)	Failure Mode
As-fabricated	501 ± 14	100	116 ± 4	92 ± 5	860	Composite
700°C/100 h	289 ± 7	~58	88 ± 3	76 ± 1	35	Brittle
1000°C/500 h	446 ± 3	~89	130 ± 2	100.5 ± 0.5	600	Composite
1100°C/500 h	432 ± 10	~86	129.5 ± 0.5	97 ± 2	670	Composite
1200°C/500 h	442 ± 17	~88	130 ± 3	106 ± 0	680	Composite

Static Fatigue of Nicalon Fiber-reinforced SiC

The effect of applied stress upon time to failure, at various temperatures, is shown in Fig. 5 for both the uncoated and coated Nicalon/SiC CFCC's. It is apparent that the uncoated material exhibits a fatigue limit, below which composite lifetimes typically were greater than 1000 h, which is dependent upon the test temperature (Fig. 5a). At 1150°C, composite lifetimes of less than 1 h are observed for applied stresses greater than 70 MPa. However, at applied stresses below 70 MPa fatigue lifetimes exceeded 100 h (tests were stopped after 600 h), although test bars exhibited a small but permanent strain after this duration. As the temperature is lowered,

the apparent fatigue stress limit increases to ~ 100 MPa. At applied stresses greater than 100 MPa the test bar lifetime was observed to increase with decreasing temperature, but decreased with increasing applied stress (Fig. 5a). It is clear that composite lifetimes of greater than 10 h, at applied stresses above 100 MPa, are only observed during static fatigue at 600°C and below. The seal coated Nicalon/SiC CFCC's had a ~ 40 μm thick SiC external coating, which was of identical composition to the SiC matrix. There is no significant difference in the matrix micro-cracking stress between the uncoated and coated materials due to the compositional similarity of the matrix and seal coat. During fatigue at 950°C, only minimal improvement in composite lifetime is observed for samples with the CVD seal coating (Fig. 5b), demonstrating that it does not provide any significant protection under these operating conditions. However, at 425°C, an order of magnitude increase in lifetime is observed relative to the uncoated material (Fig. 5b).

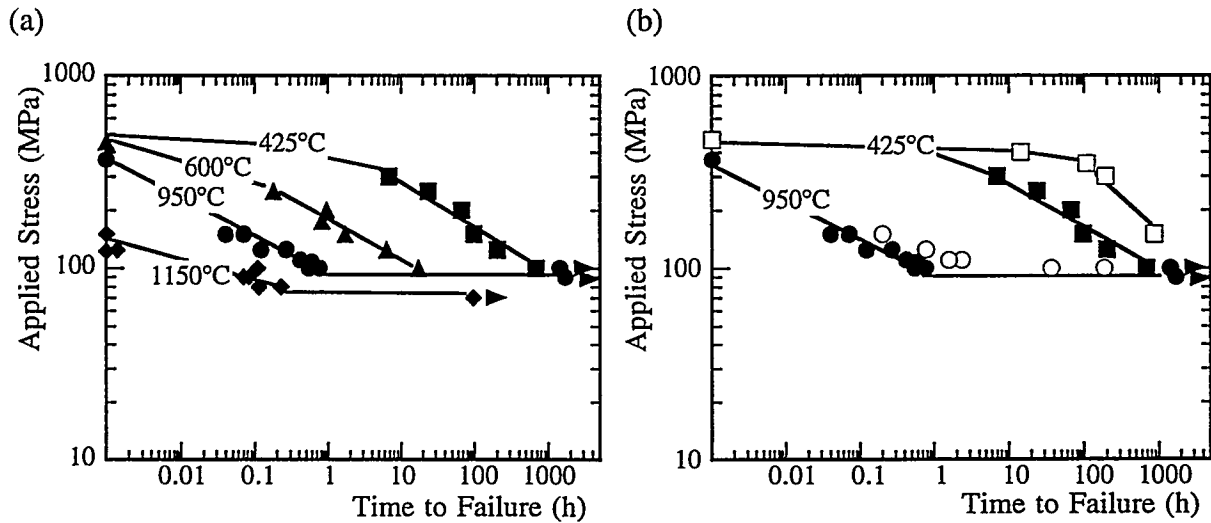


Figure 5. The effects of applied static fatigue stress upon composite lifetime, at various temperatures, for a) uncoated Nicalon/SiC and b) coated Nicalon/SiC (data for uncoated material is shown for comparison). Filled symbols represent uncoated Nicalon/SiC, and open symbols represent CVD SiC coated Nicalon/SiC.

When the uncoated material is subjected to stress during heat-treatment at temperatures of 950°C and above, negligible fiber pull-out is observed near the tensile surface of the test bar. Oxidation products are formed at the fiber/matrix interface, namely SiO_2 , which will ultimately produce a strong fiber/matrix bond. This results in a significant increase in both the interfacial debond energy and frictional sliding stress [16]. Similar observations have previously been made for the aging behavior of a Tyranno/BMAS fiber composite, where the formation of a SiO_2 bonded interface results in an order of magnitude increase in both of these interfacial parameters [12,13]. At temperatures of 600°C and below, fiber pull-out is observed in the tensile surface region (Fig. 6a), and the amount of fiber pull-out increases with both increasing applied stress and decreasing test temperature. It is apparent from Fig. 6a that the graphite interlayer is removed from this region during fatigue, however the interlayer was intact in the core region (>500 μm from the tensile surface), and near the compressive face (Fig. 6b).

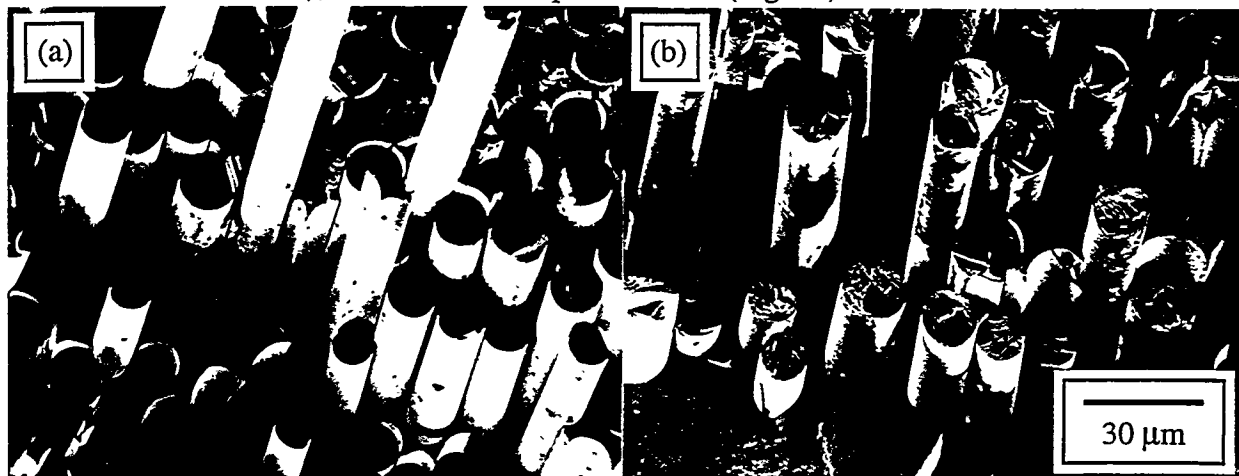


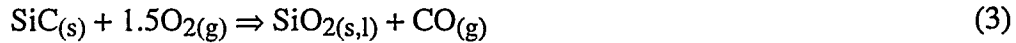
Figure 6. The fracture surface of a SiC/Nicalon tested at 600°C for 20 h; a) graphite interlayer removal in the tensile region and b) interlayer retention in the compressive region.

DISCUSSION

It is clear from the present work, as well as previous studies [8-14], that exposure to elevated temperature oxidizing environments has a detrimental effect upon the mechanical performance of CFCC's with graphitic fiber/matrix interlayers. At the lower aging temperatures, from 375 to 600°C, oxidative removal of the carbon interlayer can occur. Although the reaction is likely to be sluggish, it was demonstrated by SAM analysis on Nicalon/CAS, that carbon removal can occur to depths of at least 500 µm after 100 h exposure at 450°C in air. At higher temperatures (i.e. 700 to 800°C), there is evidence for the formation of a surface SiO₂ rich layer on the Nicalon fibers, with minimal carbon retention in the near surface region (up to 500 µm from the surface). Oxidation of the carbon interlayer will proceed by either of the following mechanisms;



At the lower temperatures (i.e. 450°C), surface oxidation of the Si-C-O Nicalon fiber will be extremely slow, and consequently oxidation of the carbon can continue indefinitely whilst the material is held at these temperatures. At higher temperatures (i.e. 600°C and above) oxidation of the fiber can occur by either of the following;



It can thus be seen that there are two competing oxidation processes occurring in the intermediate temperature range (i.e. 600-800°C), namely oxidation of the carbon interlayer and oxidation of the surface of the fiber. Oxygen transport down the annular pore (and also CO or CO₂ transport out of the pore) is controlled by a combination of molecular and Knudsen diffusion, with the relative contribution of each determined by the pore dimensions, temperature and pressure. The thermal dependence of these two processes are both lower than that controlling the oxidation of the Si-C-O fibers [17], and hence as the temperature is increased fiber oxidation will begin to dominate over oxygen transport down the annular pore. When this occurs the pore will become sealed by SiO₂ formation at the surface, and oxygen transport down to the graphitic interlayer will cease. At temperatures above 800°C surface sealing of the exposed fibers occurs rapidly in the case of Nicalon/CAS, which results in protection of the remainder of the graphitic interlayer from further oxidation. Indeed, the use of a short duration, high temperature pre-treatment at 1000°C (for between 1 to 4 h) has been shown to essentially prevent property degradation during subsequent aging at 700°C [18].

For the case of Nicalon/SiC composites with a carbon interlayer, Huger *et al* have determined the critical time (t_c) for blocking the surface connected porosity, via the formation of SiO₂ during oxidation [19];

$$t_c = \frac{1}{B_f} \left[\frac{H}{\left(1 - \frac{1}{\theta_f}\right) + R \left(1 - \frac{1}{\theta_m}\right)} \right]^2 \quad (5)$$

where B_f is the parabolic rate constant of the fiber, H is the carbon phase thickness, R is the ratio of the thickness of the oxide scales on the matrix and fiber, and θ_f and θ_m are the relative volume expansion coefficients of the fiber and matrix during oxidation to silica (1.48 and 2.3 respectively). This simplifies to;

$$t_c = \frac{1}{B_f} \left[\frac{H}{\left(1 - \frac{1}{\theta_f}\right)} \right]^2 \quad (6)$$

in the case of Nicalon/CAS, as the matrix is not oxidized (i.e. $\theta_m = 1$). Based upon the oxidation kinetics of Nicalon fibers [20], it is possible to estimate the critical surface blocking time (t_c) for Nicalon/ CAS based upon the use of Eqn. 6, and this data is shown in Table II.

Table II. Parabolic rate constant (B_f) for Nicalon fibers (estimated from [20]) and the calculated critical surface blocking time (t_c) for Nicalon/CAS at various temperatures, assuming a 45 nm graphite interface. Typical errors for the determination of t_c are of the order of $\pm 25\%$, due to the error associated in extrapolating the values of B_f from [20].

Oxidation Temp.	700°C	800°C	900°C	1000°C	1100°C	1200°C
B_f (nm ² /min.)	12.3	26.4	32.6	57.7	99.2	195.8
t_c (hours)	26	12.1	9.8	5.5	3.2	1.6

When aging in a typical laboratory environment, it is apparent that the sealing time is nearly an order of magnitude shorter. For example during pre-treatment of Nicalon/CAS, surface sealing was determined to occur after approximately one hour when pre-treating at 1000°C [18]. It is likely that this discrepancy is due to increased oxidation rates in the presence of environmental moisture, as the TGA data of Huger *et al* was obtained using dried air [20]. Consequently, further work is required to determine the effects of environmental moisture upon the oxidation kinetics of both the Nicalon fibers and the CFCC's studied.

In the present case mechanical testing after aging was performed in flexure, with the Nicalon/CAS composite having a [0,90]_{3S} ply lay-up (with ply thicknesses of ~200 μ m). Consequently, it can be seen that even if interface degradation only occurs to a depth of 500 μ m (as shown by SAM), this will have a significant effect on the outer tensile ply and hence the flexure properties of the composite. At the lower oxidation temperatures (i.e. 450°C), the graphitic interlayer is oxidized and effectively removed from the surface zone. The coefficient of thermal expansion (CTE) mismatch between fiber and matrix (Nicalon $\sim 3.1 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$, anorthite $\sim 4.5\text{--}5.0 \times 10^{-6} \text{ }^\circ\text{C}^{-1}$), coupled with the residual clamping stress on the fiber after cooling from the fabrication temperature, will cause the matrix to contract down onto the fiber after aging (under cooling). In this instance it can be expected that the debond energy will decrease, as there is no longer a chemical bond between the fiber and matrix (i.e. the carbon interlayer is removed), but the sliding stress will increase, due to frictional asperities (i.e. fiber surface roughness). These predictions have been confirmed by fiber push-down after these aging treatments [14], however further work is necessary in this area to more fully understand the effects of residual stress and fiber roughness. At higher temperatures (i.e. 700 to 800°C), the interface can become SiO₂ bonded, and both the interfacial debond energy and sliding stress increase [14], resulting in a further degradation of mechanical properties.

Although this discussion has been primarily related to degradation in the Nicalon/CAS CFCC, the comments made are also applicable to the Nicalon/SiC material. The thicker graphitic interlayer in this material (300 nm rather than 40-50 nm in Nicalon/CAS) will actually increase the *effective* intermediate temperature range over which oxidative degradation can occur, as surface sealing of the exposed fiber ends will ultimately require higher temperatures. This behavior has already been noted by Frety *et al* [21], who demonstrated that CVI SiC/SiC composites with thick carbon interfaces (140 to 200 nm) exhibit degradation when aging at both 800 and 1400°C, without applied load. Conversely, materials with a thin carbon interface (35 to 70 nm) exhibited degradation at the lower temperature, but showed minimal property degradation when aging at 1400°C, even after 1000 h, due to a surface sealing phenomenon similar to that observed in the Nicalon/CAS material used in the present work and also the Tyranno/BMAS composite studied previously [12]. It is clear from the present observations that surface sealing allows the retention of properties comparable to the as-fabricated material for Nicalon/CAS.

SUMMARY

The effects of environmental exposure upon the mechanical performance of two CFCC's have been assessed. The following conclusions can be drawn from this work;

- A commercially available glass-ceramic matrix composite, Nicalon/CAS, has been subjected to (unstressed) thermal aging treatments between 375 and 1200°C, for up to 500 hours. Thermal exposure results in considerable property degradation at intermediate temperatures, from 450 to 800°C. 'Pipeline' oxidation results in the partial removal of the carbon interlayer between the fiber and matrix when aging in this temperature range.
- The Nicalon/CAS CFCC demonstrates minimal degradation during aging at temperatures between 1000°C and 1200°C, due to the rapid formation of protective SiO₂ plugs at the

exposed fiber ends, which prevent further oxygen ingress to the fiber/matrix interface. After aging at 1200°C for 500 h, room temperature strengths of ~88% of that of the as-fabricated composite were retained. 'Ductile' composite failure modes were observed after this extended aging heat-treatment.

- Static fatigue tests were performed on a Nicalon/SiC CFCC at temperatures from 425 to 1150°C. The material was tested both with and without a CVD SiC seal coating. The fatigue life of the uncoated composite decreased with increasing applied stress and/or test temperature. A fatigue limit of ~100 MPa was observed at temperatures ≤950°C, however this was reduced to ~70 MPa at 1150°C. The composite lifetime is largely determined by oxidative removal of the thick (300 nm) graphitic interlayer at low temperatures (425 and 600°C), and by a combination of interlayer removal and the formation of strong SiO₂ bonds (formed by oxidation of the SiC matrix and the Nicalon fiber) at higher temperatures.
- The application of a SiC seal coating increases the fatigue lifetimes by an order of magnitude at 425°C, demonstrating that the interlayer oxidation reaction is significantly inhibited at this temperature. Conversely, negligible benefits were apparent during static fatigue at 950°C, with lifetimes being similar to the uncoated material.

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