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INTERFACE DEGRADATION IN CAS/NICALON DURING ELEVATED TEMPERATURE AGING

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ABSTRACT

A CaO-Al_2O_3-SiO_2 (CAS)/Nicalon glass-ceramic matrix composite has been subjected to elevated temperature oxidation heat-treatments between 375 and 1200°C, for up to 100 hours. Micro- and macro-mechanical properties have been determined by fiber push-down, using a mechanical properties microprobe, and flexure testing, respectively. Aging between 450 and 800°C results in significant property degradation, with reduced bending modulus and flexure strength, increased fiber sliding stress, and a transition to a purely brittle failure mode. Aging degradation is due to oxidative removal of the carbon interlayer, with the subsequent formation of a silica bond between fiber and matrix. At higher temperatures, carbon is retained due to the formation of a protective silica plug at exposed fiber ends, with the subsequent retention of composite properties. Short duration pre-treatment schedules, at 1000 or 1100°C, were developed to prevent intermediate temperature property degradation.

INTRODUCTION

The mechanical performance of continuous fiber reinforced ceramic matrix composites (CMC's) is primarily dependent upon the behavior of the matrix/fiber interface.[1,2] The development of a 'weak' interface results in a composite fracture resistance far exceeding that of the matrix alone. The majority of currently available CMC's utilize off-stoichiometric, polymer derived silicon carbide (SiC) fibers, such as Nicalon (Nippon Carbon Co.) or Tyranno (UBE Industries). The desired 'weak' interfaces are typically carbon based, and are either grown *in-situ*, in glass-ceramic matrix composites (GCMC's),[3-6] or applied to the fiber by chemical vapor deposition (CVD) for matrices deposited by chemical vapor infiltration (CVI).[7] An alternative interface material is boron nitride, again applied by CVD methods, typically with a CVD SiC 'overcoating' to prevent matrix diffusion through the interface to the fiber.[8]

Although carbon interfaces in GCMC's result in favorable room temperature mechanical behavior, the benefits are diminished during fast-fracture at elevated temperatures (>800°C), when rapid oxidation of the interface can occur.[5,6,9] It has also been demonstrated that oxidative aging degradation occurs during extended exposure at temperatures of the order of 600 to 900°C.[9-11] In this instance oxidative removal of the carbon interface precedes the formation of a strong SiO_2 bond between matrix and fiber, due to oxidation of the SiC fiber. However, very little work has been performed to determine the interfacial stability during extended duration aging at lower temperatures. The present paper reports upon the effect of oxidative exposure on the micro- and macro-mechanical behavior of a commonly studied GCMC over a wide temperature range (375-1200°C).

DISCLAIMER

EXPERIMENTAL PROCEDURE

The material selected for the present study is a cross-ply $[0,90]_{3S}$, $CaO\text{-}Al_2O_3\text{-}SiO_2$ (CAS)/Nicalon fiber GCMC (Type II), supplied by Corning (NY, U.S.A.). Aging heat-treatments were performed in air on machined test bars (dimensions 50 x 3.5 x 2.35 mm), at temperatures between 375 and 1200°C, for up to 100 hours. Pre-treatment, designed to inhibit intermediate temperature aging effects, was performed in air at either 1000 or 1100°C, for up to 24 hours, and was followed by aging at 700°C for 100 hours. Flexure testing was conducted on as-received and heat-treated test bars in three-point bend (40 mm outer span, giving a span-to-depth ratio of ~17:1), at a cross head speed of 0.5 $mm.min^{-1}$. Matrix/fiber interfacial properties were determined using a mechanical properties microprobe, housed within a scanning electron microscope (SEM). Microstructural characterisation was performed by scanning Auger microscopy (SAM), SEM and transmission electron microscopy (TEM), with both electron microscopes equipped with energy dispersive X-ray (EDX) analysis.

RESULTS AND DISCUSSION

Effects of Aging Exposure on the As-received Composite

The as-received CAS matrix is devitrified to anorthite ($CaAl_2Si_2O_8$), with a small volume of zircon ($ZrSiO_4$) also present, primarily at the matrix/fiber interface. A typical 'carbon-rich' matrix/fiber interlayer is shown in Fig. 1, with associated windowless EDX spectra. The interlayer thickness is approximately 45-50 nm, and was consistent for all observed interfaces in this sample. Micro-diffraction demonstrates an 'arc-like' C_{002} ring characteristic of turbostratic carbon,[12] indicating that the carbon (0001) basal plane lies parallel to the fiber surface in a manner similar to CVD carbon coatings.

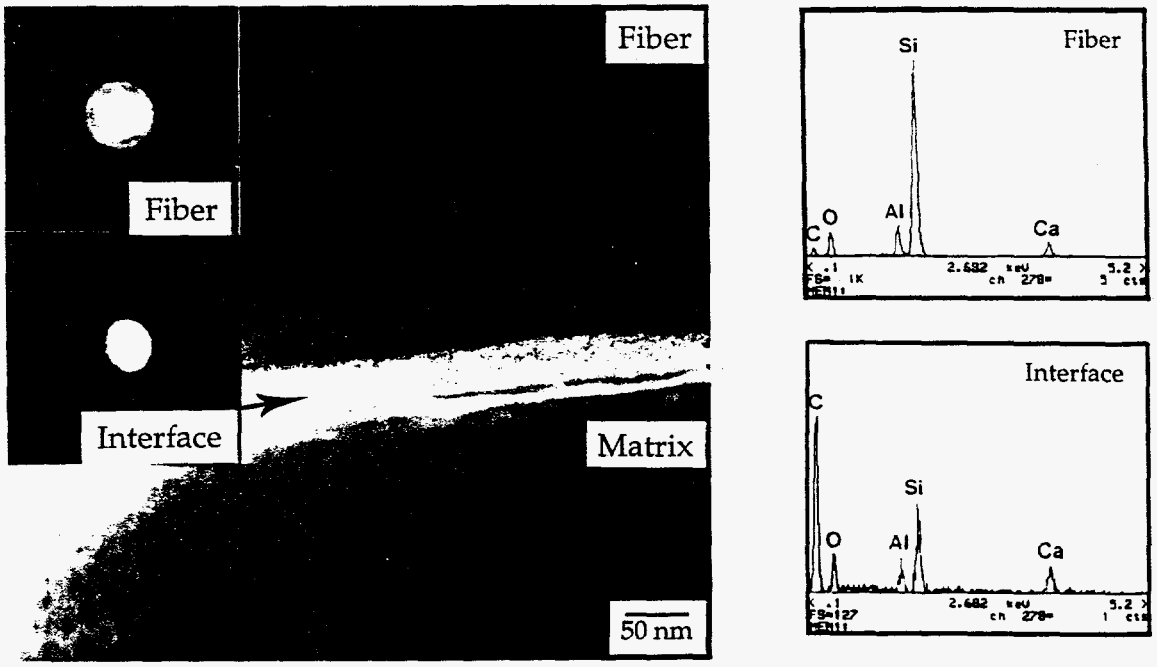

Figure 1. Bright field TEM micrograph of the 'carbon-rich' interlayer, with associated EDX spectra and micro-diffraction patterns from both fiber and matrix (inset).

The effects of aging at temperatures between 375 and 1200°C, upon both the flexure strength (σ_{UBS}) and proportional limit (σ_{PL}), are shown in Fig. 2. Significant strength degradation occurs when aging between 450 and 1000°C (Fig. 2a). A reduction in the value of σ_{PL}, which corresponds closely with the microcracking stress in the present material, occurs at temperatures as low as 375°C, with a significant reduction at 450°C (Fig. 2b). Although reasonable strength retention occurs at temperatures up to 450°C, a transition from a composite failure mode to one of brittle fracture occurs at this aging temperature (Fig. 3a). Brittle failure occurs for all subsequent aging temperatures up to 800°C (Fig. 3a). Aging at 1000°C and above, results in a reverse transition, with composite failure behavior similar to the as-received material (Fig. 3b).

(a) (b)

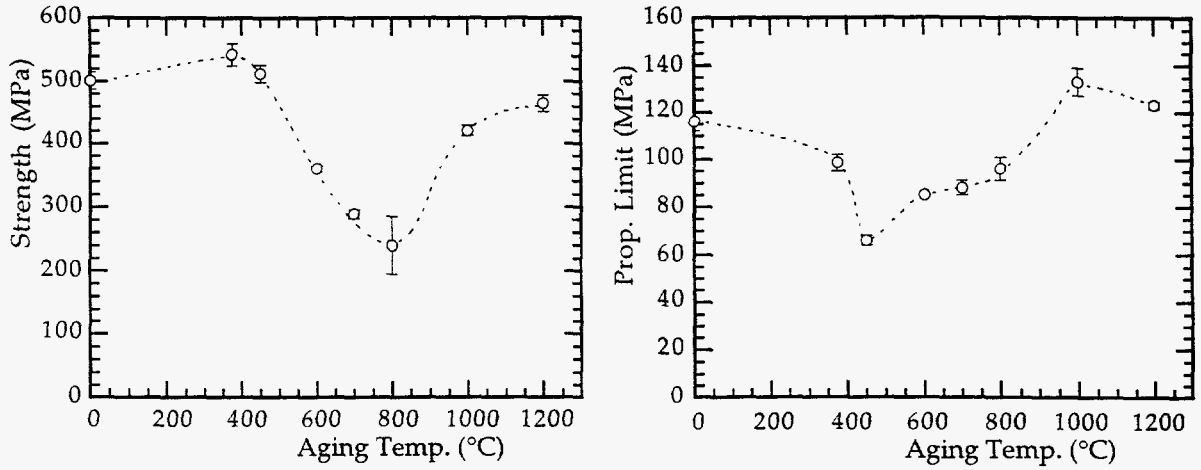

Figure 2. The effects of aging heat-treatment (for 100 hours) upon (a) the ultimate bend strength, and (b) the proportional limit, for CAS/Nicalon. A minimum of two tests were performed for each heat-treatment condition.

(a) (b)

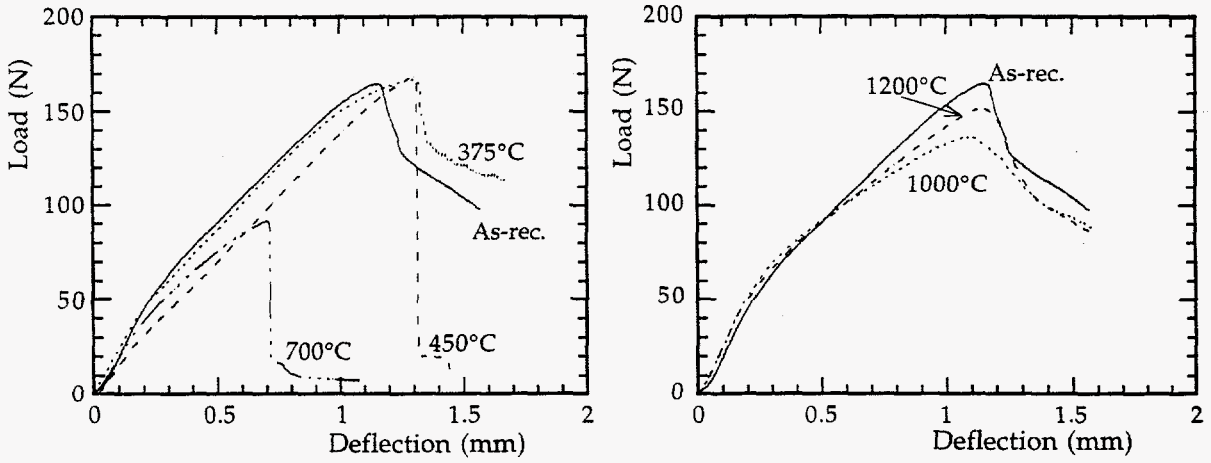

Figure 3. The effects of aging (for 100 hours) upon the load/deflection behavior of CAS/Nicalon; aged at (a) 375, 450 and 700°C, and (b) 1000 and 1200°C. Data for as-received material is shown for comparison.

These observations are generally consistent with those previously noted for a BaO-MgO-Al_2O_3-SiO_2 (BMAS)/Tyranno composite.[9] TEM confirms the removal of the

carbon at intermediate aging temperatures, with the formation of SiO_2 bonds between fiber and matrix. At higher temperatures (1000°C and above) flexure strengths comparable to the as-received material are apparent. The retention of carbon at the matrix/fiber interface is confirmed by TEM, due to the formation of protective SiO_2 'plugs' at exposed fiber ends as previously noted.[9,11] Change in interface behavior is also demonstrated by measurement of the debond energy and sliding stress (Table I).

Sample	Debond Energy* ($J.m^{-2}$)	Sliding Stress* (MPa)	Flexure Strength (MPa)	Prop. Limit (MPa)	Failure Mode
As-received	5.4 ± 1.2	24 ± 2	501 ± 14	116 ± 4	Composite
450°C/100hrs.	2.8 ± 1.5	45 ± 2	512 ± 13	66 ± 2	Brittle
600°C/100hrs.	3.1 ± 2.5	128 ± 129	360 ± 5	85 ± 0	Brittle
750°C/100hrs.	8.3 ± 11.5	196 ± 170		Not determined	
900°C/100hrs.	18.4 ± 4.4	18.6 ± 1.5		Not determined	
1200°C/100hrs.	5.0 ± 1.0	21 ± 3	464 ± 13	123 ± 2	Composite

Table I. The effects of various aging heat-treatments upon micro- and macro-mechanical behavior. *Interfacial parameters determined by *in-situ* SEM fiber push-down.

The drop in debond energy when aging at 450°C is due to the removal of the carbon interface by oxidation (determined by SAM), such that when the sample is cooled from the aging temperature the matrix 'clamps' down on to the fiber. The fiber is therefore 'easy' to debond but resists significant movement due to increased roughness effects (i.e. an increased frictional sliding stress). At higher aging temperatures a SiO_2 bond is formed between the fiber and the matrix, increasing both the debond energy and sliding stress. Brittle failure modes are consequently noted for these heat-treatment conditions. Aging above 900°C results in the retention of interfacial properties similar to the as-fabricated material (Table I), due to the formation of a protective SiO_2 'plug' on exposed fibers as previously mentioned. This effect can be utilized as a method of protecting the material, as described in the following section, where samples are subjected to a short duration, high-temperature heat-treatment designed to seal the surface and inhibit oxygen ingress at intermediate temperatures.[13]

Effects of Pre-treatment upon Aging Degradation

Pre-treatment at 1000°C provided optimum strength retention after subsequent aging at 700°C (Fig. 5a), indicating near-complete sealing of the exposed fiber ends. This results in the retention of composite failure modes after subsequent aging at 700°C for 100 hours (Fig. 5b). Retained strengths were low for short pre-treatments at 1100°C, and increased with the pre-treatment duration (Fig. 5a). This behavior was coupled with a transition from a delamination/shear-type fracture mode to one of tensile-composite failure. Delamination tended to occur upon on the outermost tensile ply, causing a sudden load drop, followed by composite failure, with high ductility (Fig. 5b). In this instance the outer ply exhibited minimal fiber pull-out, whilst pull-out was evident from the inner plies. Extending the pre-treatment time reduced this effect although tensile ply pull-out lengths were always shorter than those for test specimens pre-treated at 1000°C.

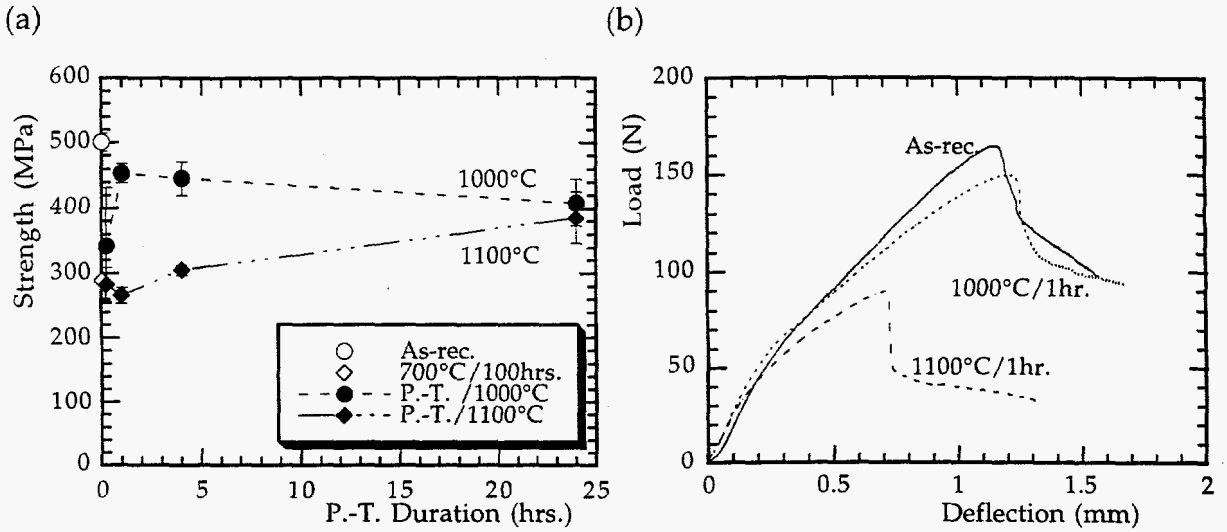

Figure 5. (a) The effects of high-temperature pre-treatment (P.-T.) upon flexure strength. (b) Load/deflection traces demonstrate the benefits of pre-treatment at 1000°C.

After pre-treatment at 1000°C, the initially exposed surface fibers (Fig. 6a) are completely sealed (Fig. 6b). However at 1100°C 'bubbles' are apparent in the low viscosity silica scale formed over the exposed fibers (Fig. 6c). SEM showed that 'bubble' concentration decreased with increasing pre-treatment duration, such that only a few were retained after 24 hour pre-treatment. The 'bubbles' must be constantly forming and sealing, as only minimal strength degradation occurs during long term aging at 1100°C. For the shorter pre-treatment durations at 1100°C, open channels must be retained after subsequent cooling to room temperature (i.e. prior to 700°C aging), allowing oxygen ingress to the fiber matrix interface. Surface sealing at 1100°C appears to be only successful for the exposed fiber ends and not the surface fibers, hence the tendency for brittle failure of the outer tensile ply followed by composite failure for all the inner plies. Conversely pre-treatment at 1000°C (for between 1 to 4 hours) does appear to be a suitable, and simple, method for inhibiting intermediate temperature degradation provided the material is utilized below the microcracking stress, which in the case of CAS/Nicalon is relatively low (~115 MPa for the as-received material).

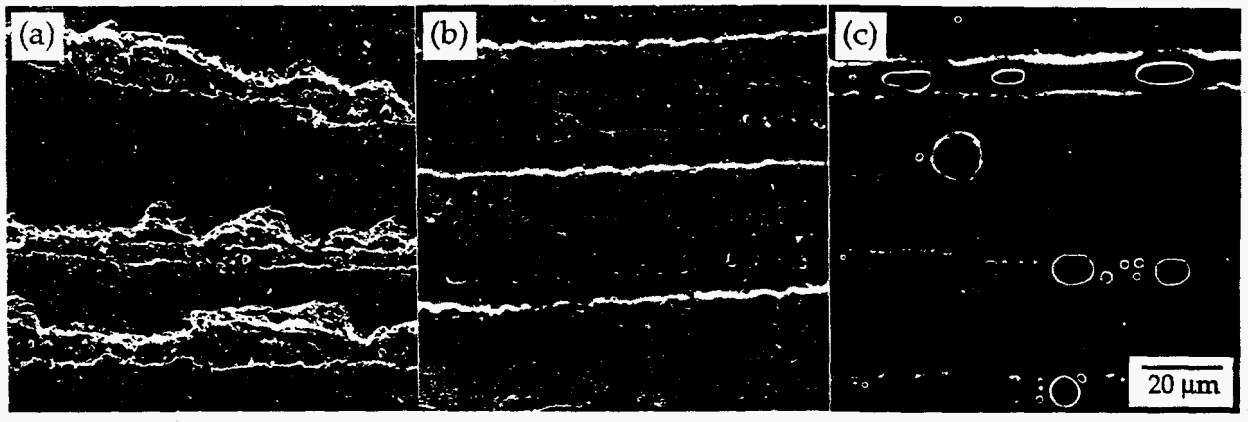

Figure 6. SEM micrographs of the tensile surfaces of (a) the as-received CAS/Nicalon composite, and samples pre-treated at (b) 1000°C for 4 hours and (c) 1100°C for 4 hours, followed by aging at 700°C for 100 hours.

CONCLUSIONS

The present study has demonstrated that oxidative exposure of CAS/Nicalon GCMC's results in property degradation at temperatures as low as 375°C, with severe degradation occurring when aging between 450 and 900°C, due to 'pipeline' oxidation of the carbon interface. At 750 and 900°C a strong fiber/matrix bond is created through oxidation of the Nicalon fiber surface to form SiO_2. At higher temperatures (1000 to 1200°C) protective SiO_2 'plugs' are rapidly formed at the exposed fiber ends, which results in the prevention of further carbon loss. This protection mechanism allows extended exposure (up to 100 hours) at temperatures as high as 1200°C with minimal loss of strength or ductility, with flexure strengths ~85-92% of those for the as-received material. Optimal pre-treatment schedules (i.e. 1000°C for one to four hours) were found to be beneficial for preventing subsequent intermediate temperature aging degradation, via the formation of a protective SiO_2 'plug'.

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