MECHANICAL BEHAVIOR OF A HI-NICALON™/SIC COMPOSITE HAVING A POLYCARBOSILANE DERIVED MATRIX

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ABSTRACT

Polymer infiltration of a rigidized preform, followed by pyrolysis to convert the polymer to a ceramic, potentially offers a lower cost alternative to CVD. It also offers more moderate temperature requirements than melt infiltration approaches, which should minimize potential fiber damage during processing. However, polymer infiltration and pyrolysis results in a more microcracked matrix. Preliminary mechanical property characterization, including elevated temperature (1204°C) tensile, 500 h stress rupture behavior and low cycle fatigue, was conducted on Hi-Nicalon™ /Si-C-(O) composites having a dual layer BN/SiC interface and a matrix derived by impregnation and pyrolysis of allylhydridopolycarbosilane (AHPCS). Microstructural evaluation of failure surfaces and of polished transverse and longitudinal cross sections of the failed specimens was used to identify predominant failure mechanisms. In stress rupture testing at 1093°C, the failure was interface dominated, while at 1204°C in both stress rupture and two hour hold/fatigue tests failure was matrix dominated, resulting in specimen delamination.

INTRODUCTION

Allylhydridopolycarbosilane (AHPCS), whose structure is shown in Figure 1, produces near-stoichiometric SiC with char yield of greater than 75% on pyrolysis
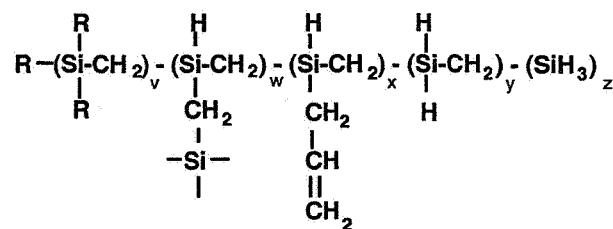

Figure 1: Nominal structure of AHPCS

to moderate temperatures. [1-5] As with other polymer-derived ceramics, pyrolytic conversion is accompanied by sizeable volume changes, requiring repeated infiltration and pyrolysis cycles for matrix densification. In a multi-ply layup material, matrix shrinkages are accompanied by cracking transverse to the fiber plies, as the dimensions of the entire composite change during pyrolysis. By infiltrating a rigidized preform material, the preform itself does not shrink. If the interface is sufficiently weak, the matrix breaks into blocks, or islands, around which additional precursor can be infiltrated. This results in a matrix which is microcracked on fabrication.

An eight ply five harness satin weave Hi-Nicalon™ fabric coated with a dual BN and SiC interface coating (Dupont Lanxide Composites, Inc., Newark, Delaware) was chosen for the preform architecture. Composite panels were produced by infiltration of the preform, cure, pyrolysis and reinfiltration.

The objective of this study was to perform a preliminary examination of this material to better define the time/temperature regime for a more detailed examination of its upper use temperatures, lifetimes and stress capabilities in aggressive environments. Preliminary characterization was in air. Stress levels were selected based on fast fracture tensile stress-strain behavior at 1204°C. Stress rupture and low cycle fatigue tests were performed on a very small number of samples taken from a single panel. Thus, the results are useful for elucidating failure mechanisms, but should not be viewed as characterizing mechanical properties of the material.

EXPERIMENTAL

Rigidized preforms were comprised of nominally 40 volume percent Hi-Nicalon™ fiber, coated with chemical vapor infiltration (CVI) deposited BN (approximately 0.8-1.0 μm), overcoated with 20-30 μm of SiC, and having roughly 21-23% open porosity. AHPCS having 5 % allyl groups, based on Si content, and manufactured from a precursor having 15% dichlorosilane was used as the preceramic polymer. Two panels were fabricated by Starfire Systems, Inc.; one was cured in an autoclave, and one cured at ambient pressure. Both were infiltrated, cured, pyrolyzed to a temperature of 1000°C, and reinfiltrated, for a total of ten processing cycles. Polished cross sections of the as-fabricated composites showed higher matrix density and more uniform microstructure in the autoclaved material than in the panel processed at ambient pressure. For this reason, the autoclaved panel was selected for stress rupture and low cycle fatigue characterization.

Tensile fast fracture, stress rupture and two-hour hold fatigue tests were used to assess the mechanical properties of the composites. Five 150-mm long tensile bars with a gage length of 28 mm and width of 10 mm were machined from each

test panel. Additional machining details for the tensile bars are described by Worthem.[6] A predefined run-out life of 500 hours was selected for both the stress rupture and two-hour hold fatigue tests. The fast fracture loading rate was 10 MPa/sec. All mechanical tests were performed on electro-mechanical test machines with water-cooled wedge grips. Test machine alignment was calibrated to have less than 5% bending. Specimen heating was conducted with inductively heated SiC susceptors under closed-loop control within +/-1% using Type R thermocouples. Each specimen was subjected to a temperature dwell time of 10 minutes prior to testing.

Metallographic examinations of failed specimens were performed to assess environmental damage mechanisms. Based on results from previous damage mechanism studies[7] metallography samples were sectioned from the end opposite the fracture surface equidistant from the gage section center. This procedure insures that the temperature profile of the examined piece mirrors that near the fracture surface, and that the existing damage has not been influenced by post failure exposure of the fracture.

RESULTS AND DISCUSSION

A polished cross-section of the as fabricated composite is shown in Figure 2. The BN interphase is seen as the dark gray area surrounding individual fibers. Fiber tows are encapsulated with 20-30 μm of CVI SiC. Porosity within the tow
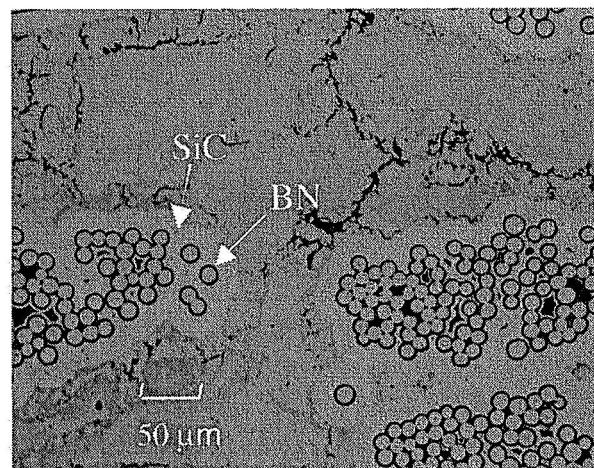

Figure 2: As fabricated composite.

bundle is closed off from the composite surface. Between tow bundles are matrix rich areas having large blocks of material from the first infiltration cycle which are uncracked. Regions between the large matrix blocks are filled with material from successive infiltrations. The matrix derived from these later infiltrations differs in

gray level, and probably density, from the initially infiltrated material, and appear more microcracked. The different gray levels correspond to differences in relative oxygen content of the Si-C-O matrix, as determined by energy dispersive spectroscopy (EDS), with the darker shaded areas having the relatively higher oxygen concentrations, and presumably, the lower densities, as they have experienced fewer pyrolysis cycles. Oxygen level in the starting polymer is extremely low; incorporation of more oxygen in later cycles is the result of moisture pick-up during handling.

Initial tensile tests were performed in fast fracture at 1204°C on specimens from both the autoclaved and free standing cure panels. Stress-strain curves were highly consistent in shape and ultimate stress and strain, despite the difference in void levels between the two composites.

A representative stress-strain curve is shown in Figure 3. Loading is linear to a level of about 80 MPa, where a decrease in modulus occurs. This point traditionally is considered to indicate the "matrix cracking" stress, even though the polymer-derived portion of the matrix is microcracked on fabrication. The
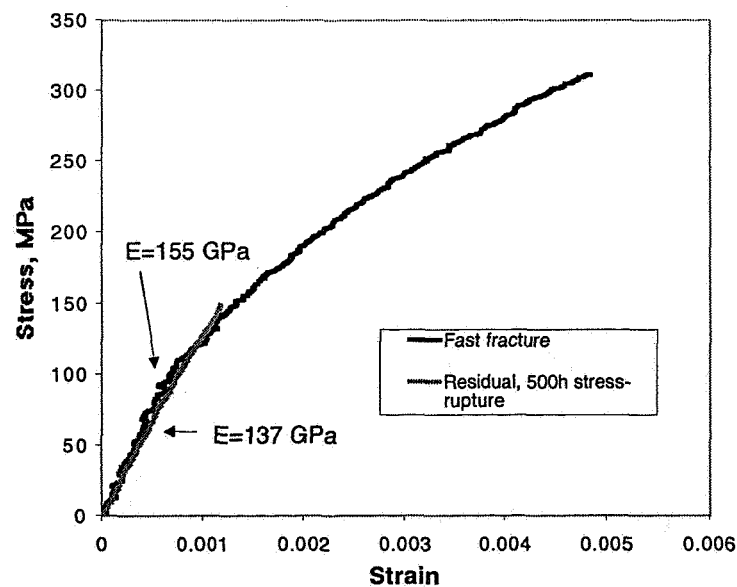

Figure 3: Representative tensile stress-strain curve, 1204°C showing fast fracture of as-received material and residual strength after 1093°C exposure.

observation of an initial linear region may be explained by stiffening of the composite from the SiC over layer, which also is a component of the matrix. Although the polymer-derived matrix component is microcracked, it maintains enough integrity to transfer load among the SiC coated fiber bundles.

By comparison, the stress-strain curve for a Nicalon/Blackglas composite, which is similarly the product of multiple infiltration and pyrolysis cycles and similarly microcracked on fabrication, but which lacks the higher modulus SiC layer, is non-linear on initial loading.[8]

Ultimate stress in fast fracture in air at 1204°C is nominally 310-315 MPa, at a strain of slightly less than 0.5 percent. Fracture surfaces exhibited significant fiber pullout.

Based on the fast fracture data, an autoclaved sample (008-3) was tested in tensile stress rupture at 1093°C and a stress level of 130 MPa, just beyond the first matrix cracking stress. The rupture test was stopped after 500 hours, and the sample fast-fractured to determine residual strength. The residual strength was found to be 148 MPa, or 48 percent of the initial strength (Figure 3). Polished cross sections of the sample taken at the mirror point from the fracture site show mechanically induced cracks running transverse to the loading direction which breech the CVI SiC layer and extend into the fiber bundles (Figure 4). Some of
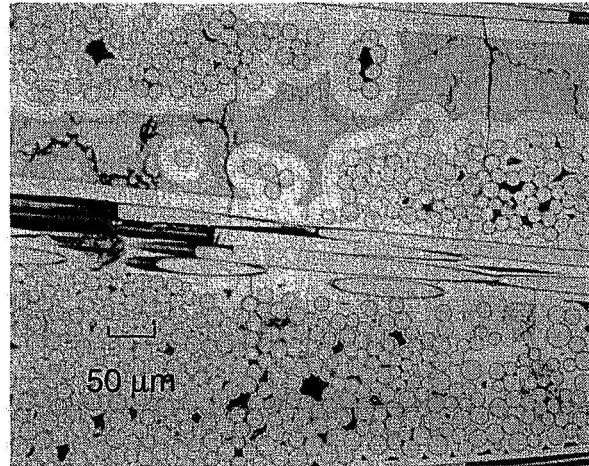

Figure 4: Specimen following 1093°C, 500h exposure, 130 MPa.

the polymer-derived matrix regions also appear to be more porous than in the as-fabricated specimens (Figure 5), suggesting possible evolution of SiO or CO from the silicon oxycarbide, while other areas remain intact. In a few areas the BN interface has disappeared, and a gap remains; in a very few areas, small regions of SiO_2 are found adjacent to the fiber.

After specimen 008-3 achieved runout, the stress level and temperature were increased to 145 MPa and 1204°C, respectively, in the next test. At the higher temperature and stress level, the new sample (008-5) failed in 9.6 hours, as compared with a 500 hour runout in the 1093°C test. Polished cross sections taken at the mirror point, as described above, exhibited a more extensive matrix
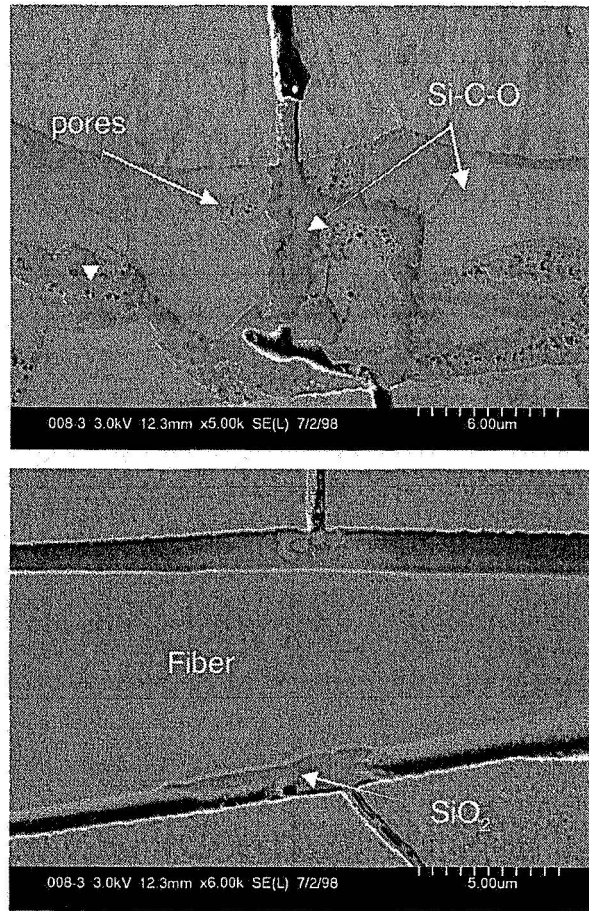
Figure 5: Sample following 1093°C, 500h exposure, 130 MPa.

breakdown. The fracture surface was characterized by an extensive delamination parallel to the load direction. SEM analysis of polished sections revealed oxidation of the BN layer, with SiO_2 formation in the interface region (Figure 6), while analysis of the fracture surface showed glassy SiO_2 "caps" on broken matrix fragments (Figure 7).

In order to assess the influence of mechanical loading on failure, one specimen was tested in two hour hold fatigue at 145 MPa, 1204°C. Failure occurred at an aggregate time of 5.2 hours, or 1.2 hours into the third cycle. A large delamination was noted parallel to the load direction. Polished sections showed extensive matrix cracking. Examination of the fracture surface indicated that the BN interface remained intact, with no evidence of oxidation.
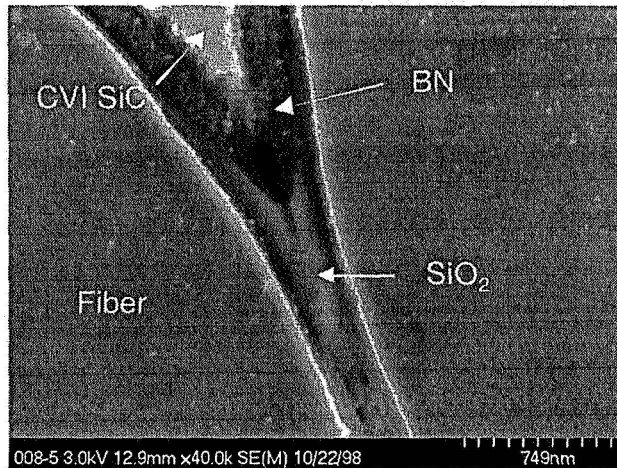
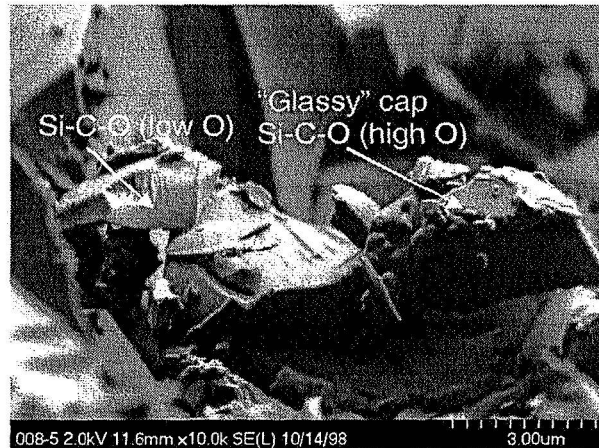**Figure 6:** Polished section of sample failed in stress-rupture at 1204°C, 145MPa.

Figure 7: Fracture surface of 1204°C, 145 MPa stress-rupture sample.

SUMMARY AND CONCLUSIONS

Of the composites fabricated for this study, the autoclaved panels exhibited the most uniform microstructure and fewest voids. These composites showed potential for hundreds of hours of life at stress levels at or below 130 MPa, where failure occurs by oxidation of the interface through cracks extending through the matrix and into the fiber bundle. At a higher stress level and higher temperature, matrix delamination and more extensive microcracking of the matrix in the fatigue test suggests the combination of stress and temperature exacerbates composite degradation. It should be noted that the elevated temperature tests

were conducted significantly above the 1000°C processing temperature. As the polymer-derived matrix continues to densify with increasing temperature, the extension of already present cracks is not unexpected, and it is likely that this also contributes to damage. If further matrix densification alone is the problem, it might be corrected by higher processing temperatures, assuming sufficiently resilient fibers However, the loss of matrix from the later infiltration cycles and evidence of volatile formation in these regions in the 500 hour sample (Figure 5) implies the possibility of matrix degradation by loss of SiO and/or CO evolution, implying the upper temperature bound for this material is below 1204°C, unless oxygen incorporation during processing can be excluded.

ACKNOWLEDGMENTS

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