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ABSTRACT

Mechanical properties of Nicalon-fiber-reinforced silicon carbide (SiC) matrix composites fabricated by a forced chemical vapor infiltration (CVI) process have been measured and compared with properties of composites fabricated by a conventional isothermal process. The mechanical properties are nearly identical for composites fabricated by the two processes provided that hot-face temperatures <1200°C are used for the forced CVI process. Composites reinforced with more stable Tyranno fibers were fabricated by forced CVI and exhibited room temperature mechanical properties similar to those of Nicalon-reinforced composites and improved high-temperature strengths.

INTRODUCTION

Composites consisting of silicon carbide (SiC) matrices reinforced with continuous silicon-carbide-oxygen (Si-C-O) fibers are being developed for many high-temperature structural applications. Chemical vapor infiltration (CVI) is an attractive process for fabricating these fiber-reinforced composites because continuous ceramic fibers can be processed without strength degradation. The great potential use of ceramic matrix composite materials has prompted in-depth investigations of these materials.

Fiber-reinforced ceramic-matrix composites have been fabricated by two distinctly different CVI processes. The first, by which most CVI composites are fabricated, is the isothermal process in which reactant gases diffuse into freestanding preforms (Fig. 1).[1-3] The second process, developed at Oak Ridge National Laboratory (ORNL), simultaneously uses a thermal gradient and a pressure gradient in which the reactant gases are forced into the cool side of the fibrous preform. Densification in the isothermal process is relatively slow in comparison with the forced-flow process because of the use of diffusive transport of gaseous reactants and reaction by-products. The reduced infiltration times offered by the forced-flow process make the ORNL process especially attractive for densifying thick-walled, simple shapes.

Unfortunately, the properties of the Nicalon fibers routinely used in both CVI processes degrade at elevated temperatures. Composites fabricated by the isothermal process are exposed to a lower processing temperature than are composites fabricated by forced CVI. Therefore, this investigation compares the mechanical properties of composites fabricated by the two processes. In addition, the mechanical properties of composites reinforced with reportedly more stable Tyranno fibers were compared with those of Nicalon-reinforced composites.

BACKGROUND

Comparison of CVI Processes

The economical densification of composites by the isothermal process requires large furnaces. To ensure uniform infiltration throughout the furnace, the isothermal process must be slowed by combinations of low-temperature, low-reactant concentrations and low pressures to avoid coating and sealing the outer surface of the preform and depleting the reactants before they reach the inner volume. The Societe Europeenne de Propulsion (SEP) has successfully commercialized this process and has licensed it to E. I. du Pont de Nemours and Company in the United States. Although the process is proprietary and specific processing conditions are unknown, the processing temperature is assumed to be ~1000°C. The composite shapes are exposed to this temperature for relatively long periods (weeks to months) during which the fibers are thought to lose some fraction (30 to 50%) of their strength.

In the forced CVI process[4-6] fibrous preforms are retained within a cylindrical graphite holder that contacts a water-cooled, metal gas distributor that cools the bottom and side surfaces of the substrate

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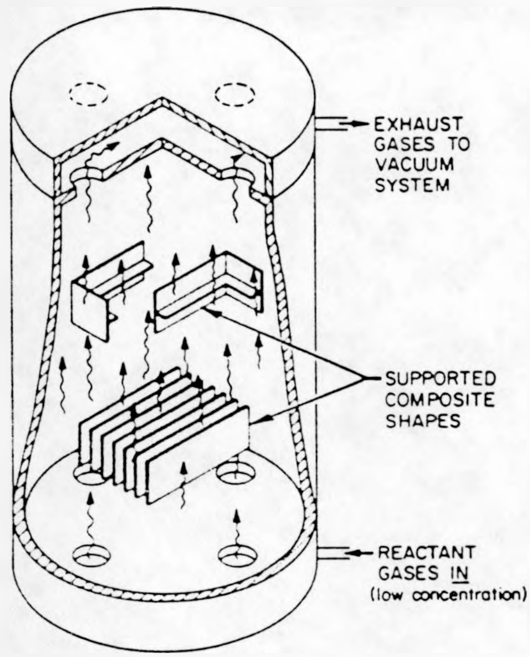

Fig. 1. Schematic representation of the isothermal CVI process. Reactant gases, as they flow through the furnace at a reduced pressure, diffuse into fibrous preforms and effluents diffuse back to the preform surface.

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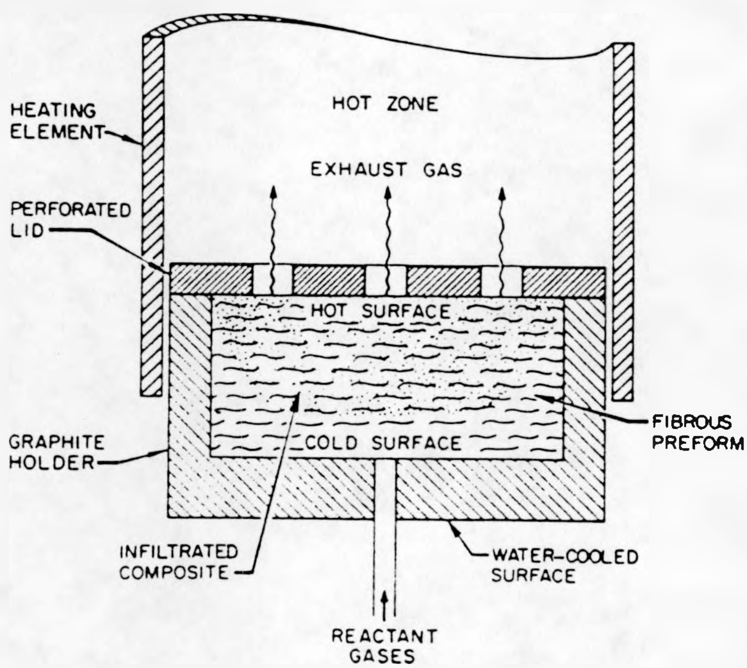

Fig. 2. Schematic representation of the forced flow-thermal gradient CVI process. Reactant gases are forced under pressure into the cooled side of the fibrous preform and flow toward the hot side, where SiC is readily deposited on the fibers.

(Fig. 2). The top of the fibrous preform is exposed to the hot zone of the furnace (normally 1200°C), which creates a steep temperature gradient through the thickness of the preform. The reactant gases are forced under pressure into the cooled side of the fibrous preform but, because of the low temperature, do not initially react. The gases flow from the cooled portion of the preform into the hot portion, where they react-depositing the matrix on the fibers. Deposition of matrix material within the hot region of the preform increases the density and thermal conductivity of the preform; therefore, the deposition zone moves progressively from the hotter regions toward the cooler regions. Composites fabricated by the forced CVI process are thus exposed to higher temperatures (1200°C compared to 1000°C) than in the conventional CVI process but for much shorter times (~24 h vs weeks or months).

Comparison of Fiber Reinforcements

The baseline fiber used by SEP for isothermal CVI processing has been ceramic-grade Nicalon, a polymer-derived Si-C-O fiber.[7-8] The fiber consists primarily of SiC, which makes it attractive for elevated temperature reinforcement. During the development of the forced CVI process, plain-weave ceramic-grade Nicalon cloth was used almost exclusively for the fabrication of composites. The strength of the fiber reinforcement in ceramic matrix composites can be directly correlated with the overall mechanical properties of the composite. Because of grain growth and the formation of large pores, the strength of the Nicalon is degraded when it is heated above 1000°C.[9-10]

As a result of the reported higher stability of Tyranno over Nicalon, Tyranno reinforcing fibers are of great interest.[11] Nippon Carbon Company reported the strengths of Nicalon to be 2900 MPa; however, strengths are reduced to about 1000 MPa by carbon coating, weaving into fabric, and annealing at 1200°C. Tow testing of Tyranno fibers determined the as-received strength to be 3500 MPa.[12] After the Tyranno fibers were carbon coated, woven into fabric and annealed to temperatures as high as 1400°C, a tensile strength of 2000 MPa was maintained.

Control of Fiber-Matrix Bonding

The mechanical properties of Nicalon-reinforced SiC composites are controlled by the strength of the bond between the fibers and the matrix. Deposition of the SiC matrix directly onto the Nicalon fibers results in a strong interfacial bond that produces brittle behavior. An intermediate coating applied to the fibers before infiltration is needed to weaken the fiber-matrix bond and produce crack deflection and fiber pullout that contribute to the "toughening" of the composite. Deposition of a carbon or boron nitride layer has been shown to produce appropriate fiber-matrix bonding to enhance fiber pullout and slip with a resultant increase in the toughness and the ultimate strength of the composite material.[12-16]

EXPERIMENTAL PROCEDURES

Preform Assembly

Fibrous preforms were assembled for the forced CVI process by stacking multiple layers of Nicalon plain-weave fabric rotated in a $0° \pm 30°$ sequence within the cavity of a graphite holder. The layers were compressed by hand to produce a preform with a nominal loading of 40 vol % fiber and were held in place by a perforated graphite lid. Two sizes of fibrous preforms were constructed, small disks (45 mm diam, 12.5 mm thick) and larger disks (75 mm diam, 16 mm thick). After assembly, preforms were precoated with thin layers (0.2 to 0.3 μm) of carbon from an argon/propylene mixture. Boron nitride coatings (0.2 to 0.3 μm thick) were applied from a mixture of boron trichloride, ammonia, and hydrogen to a few 45-mm-diam preforms.

Composite Infiltration

Preforms were infiltrated with SiC produced by the decomposition of methyltrichlorosilane (MTS) in hydrogen at elevated temperature and atmospheric pressure. A series of disk-shaped composite specimens was fabricated for our investigation of the effect of top surface temperature on the mechanical properties of the material. Composite specimens with hot-face temperatures ranging from 1100 to 1400°C were investigated, and the processing conditions are detailed in Table 1.

Table 1. Composite specimens fabricated for investigation of the effect of hot-face temperature on mechanical properties

Run	Fiber content (%)	Processing temperature (°C)	Processing time (h)
351	41.7	1100	36.0
249	39.8	1175	27.5
346	41.8	1200	19.0
247	40.9	1225	17.1
248	41.0	1275	18.0
353	41.2	1300	20.5
354	41.7	1400	9.0

Notes: All composites were fabricated from plain-weave, ceramic-grade Nicalon fabric that had been coated with a carbon interface. All samples were 45 mm diam and 12 mm thick.

A second series of composite specimens was fabricated to evaluate the effect of elevated temperatures on the mechanical properties of composite materials. Preforms consisting of carbon coated Nicalon (run 255), boron nitride coated Nicalon (run 268) and carbon coated Tyranno (run 258) were infiltrated with SiC for this investigation.

A third series of composites was fabricated from Tyranno fabric to determine their room-temperature mechanical properties. Three 45 mm diam. preforms containing ~42% carbon coated Nicalon fibers were infiltrated with SiC at 1200°C.

Flexure Testing

Flexure bars were cut with a diamond saw from the samples parallel to the 0° orientation of the top layer of cloth. Tensile and compression surfaces were ground parallel to the long axis of the specimen. The average dimensions of the test bars from the composite samples were

2.5 × 3.3 × 40 mm for the small composite samples and 3 × 4 × 55 mm for the larger composite samples.

Room-temperature flexure strengths were determined by a four-point bending method, with a support span of 25.4 mm, a loading span of 6.4 mm, and a crosshead speed of 0.0085 mm/s. Bend bars used for elevated-temperature flexure testing were first coated with a 35-μm layer of SiC to prevent oxidation of the carbon or boron nitride interlayers exposed during cutting and grinding. The elevated-temperature flexure strengths were determined by four-point bending, with a support span of 40 mm, a loading span of 20 mm, and a crosshead speed of ~0.009 mm/s. All specimens were loaded perpendicular to the layers of cloth.

The apparent fracture toughness of composites reinforced with carbon-coated Nicalon and Tyranno fibers were measured by the single-edge, notched-beam (SENB) technique. Notches were cut with a 0.25-mm blade across the width and at the center of flexure specimens (3 × 4 × 55 mm) to a depth 30% of the 3-mm thickness. The flexure bars were loaded in four-point bending (support span of 25.4 mm and a loading span of 6.4 mm).

RESULTS AND DISCUSSION

Room-temperature flexure strengths have been measured on composites fabricated by the forced CVI process.[17] The difficulties in interpreting flexure-test results for continuous fiber-reinforced composites are recognized, and the results are reported only for comparison of composites fabricated under different processing conditions. Composites fabricated before 1989 with a top or maximum temperature of 1200°C by the forced CVI process had an average flexure strength of 320 MPa. Flexure strength values were generally consistent within each composite sample (i.e., no apparent effect of location of the specimen existed with respect to the hot face of the composite).[17] These values are nearly identical to those reported by Lamicq et al.[18] for Nicalon-reinforced SiC matrix composites infiltrated at SEP by the isothermal CVI process.

Flexure strengths of typical composites fabricated more recently increased to about 380 MPa (Table 2). A slight decrease in density is observed from the top (or hot face) of the composite toward the bottom (or cold face). The reduced density of the flexure bars from the middle and bottom layers of the composite appears to decrease the flexure

Table 2. Characterization of Nicalon-reinforced composites

Sample	Fiber content (vol %)	Sample location	Composite density (% theoretical)	Flexure strength (MPa)
21	41	Top	87.2 ± 0.3	417 ± 18
		Middle	85.5 ± 0.7	406 ± 30
		Bottom	84.4 ± 0.7	390 ± 14
23	41	Top	88.2 ± 1.0	396 ± 30
		Middle	87.8 ± 0.4	354 ± 44
		Bottom	85.4 ± 1.0	308 ± 26
364	37	Top	91.8 ± 0.6	407 ± 23
		Middle	88.1 ± 0.8	345 ± 27
		Bottom	91.0 ± 1.0	339 ± 19

strength. When large numbers of samples were examined in a previous study,[17] strength was related to density but significant scatter in the data indicated that other factors also affect strength.

Apparent fracture toughness measured for composites fabricated from Nicalon cloth by the forced CVI process is 23.5 ± 2.9 $MPa{\cdot}m^{1/2}$, which is nearly identical to the room-temperature value reported by Du Pont or SEP[17] (25 $MPa{\cdot}m^{1/2}$) for isothermally produced composites. Because of the similar mechanical properties for composites fabricated by different CVI techniques, processing of composites at 1200°C by the forced CVI method must cause no greater degradation of fiber strength than processing at 1000°C by the isothermal method. Slightly higher flexure strengths (380 vs 320 MPa) reported by the forced CVI process may be the result of different cloth weaves.

Unusually low flexure strengths have been observed for composites processed at temperatures higher than 1200°C by the forced CVI technique. To investigate the effect of processing temperature on the strength of Nicalon/SiC composites prepared by forced CVI, disk-shaped samples were fabricated at top (hot) surface temperatures ranging from 1100 to 1400°C. A plot of the average flexure strengths of specimens cut from the uppermost portion (the volume that experienced the highest processing temperatures for the longest time) clearly illustrates the strength loss above 1200°C (Fig. 3). Similar attempts to correlate strengths with processing time or density, both of which spanned a narrow range, indicated no strong relationship.

During this investigation, a limited number of SiC-matrix composites were fabricated with Tyranno fibers precoated with ~0.2 μm of pyrolytic carbon (Table 3). Although composites fabricated with Tyranno fibers were not as dense as those fabricated with Nicalon fibers, the mechanical properties were approximately equal. Forced CVI processing has been optimized for the relatively open weave used at ORNL. Tyranno fibers have a diameter of 8 to 10 μm and are available in only 1500-filament tows. The smaller diameter flexible fibers form a tight bundle with little porosity, which makes them difficult to infiltrate. Optimized processing conditions would reduce the wide variation in density within the samples described in Table 3.

The mechanical properties of composites reinforced with Tyranno fibers were encouraging. Despite the somewhat less than optimum density of the fabricated composites, strengths >350 MPa were obtained for samples from the top, middle, and bottom of the composite (Table 3). Tyranno-reinforced composites exhibit "toughening" by fiber pullout. Although the fracture toughness values are similar, the fracture appears to be slightly more brittle than that of Nicalon composites.

The effect of testing temperature on the flexure strength of carbon-coated Nicalon and Tyranno fibers in a SiC matrix was investigated. The results of the elevated temperature tests are summarized in Fig. 4. A gradual increase in the strength of the Nicalon/SiC composites produced by forced CVI was observed up to a temperature of 1000°C.

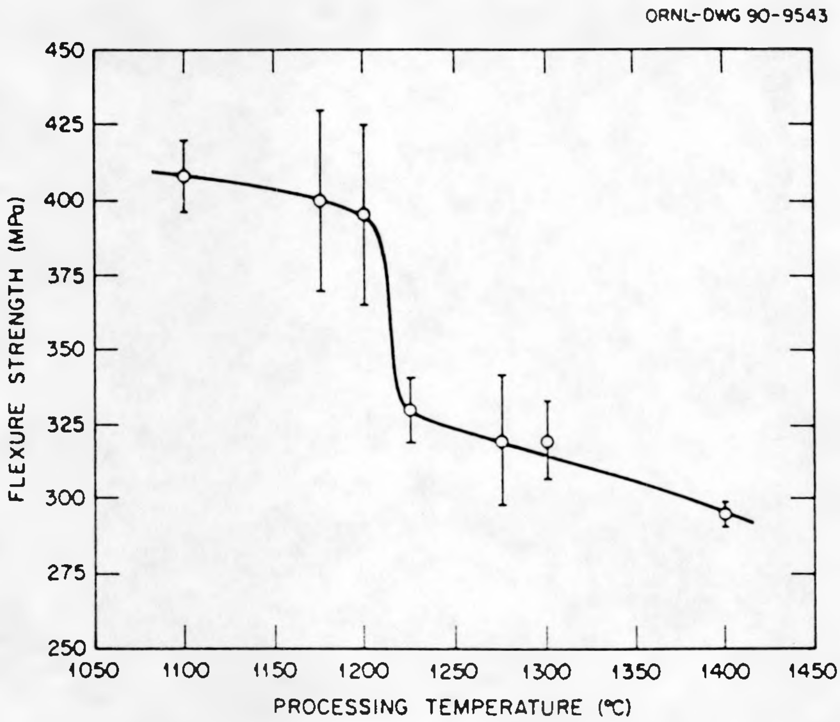

Fig. 3. Correlation of room-temperature flexure strength with processing temperature as measured on the hot face of the Nicalon-reinforced SiC matrix composite.

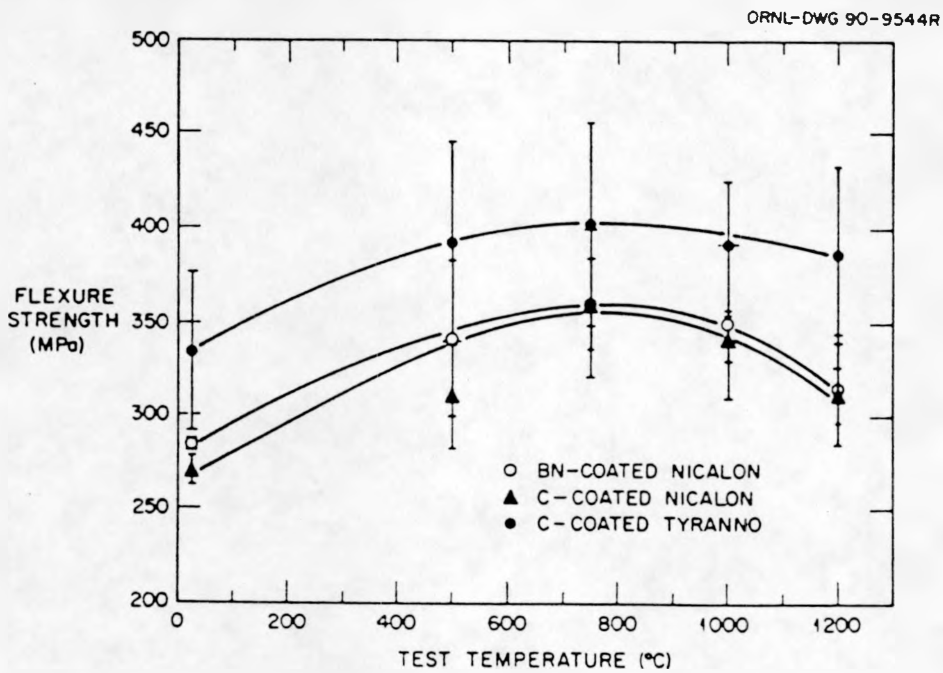

Fig. 4. Correlation of flexure strength with testing temperature for fiber-reinforced SiC matrix composites. Tyranno fibers with a carbon interface exhibit higher strengths at all temperatures than do Nicalon fibers with carbon or boron nitride interfaces.

Table 3. Characterization of composites reinforced with Tyranno fibers

Sample	Fiber content (vol %)	Sample location	Composite density (% theoretical)	Flexure strength (MPa)	Apparent fracture toughness ($MPa \cdot m^{1/2}$)
242	43	Top	79.4 ± 1.8	395.4 ± 18.4	20.9 ± 2.0
		Middle	75.6 ± 0.2	395.0 ± 7.5	20.6 ± 1.9
		Bottom	72.5 ± 0.5	351.9 ± 11.0	
243	42	Top	81.0 ± 0.7	368.9 ± 7.7	19.6 ± 1.0
		Middle	75.3 ± 0.1	364.2 ± 2.4	18.4 ± 1.8
		Bottom	64.4 ± 0.8	216.1 ± 36.5	
258[a]	40	Top	85.5 ± 0.7	388.3 ± 19.2	

[a]The middle and bottom of sample 258 used in other tests.

The composites exhibited good strengths and gradual failure in all tests. A decrease in the strength of the composites was noted above 1200°C, most likely due to the degradation of fiber properties at this temperature. These results are nearly identical to those reported by Lamicq et al. for composites produced at SEP by the isothermal CVI process.[18] The strengths of the Tyranno-reinforced composites were higher than those of the Nicalon/SiC composites at all test temperatures, and no significant decrease in flexure strength was observed above 1200°C. Additional tests at elevated temperatures and after long-term heat treatments are being performed to further characterize the high-temperature properties and the stability of the two fibers.

CONCLUSIONS

Silicon carbide matrix composites fabricated by the forced CVI process have been characterized for room-temperature flexure strength, room-temperature fracture toughness, and high-temperature flexure strength. Forced CVI composites fabricated at hot-face temperatures ≤1200°C exhibit an average flexure strength of ~380 MPa and an apparent fracture toughness of ~23 $MPa \cdot m^{1/2}$. Because these values are nearly identical to those reported by SEP and Du Pont for composites fabricated by the isothermal CVI process, apparently no additional fiber degradation results from the higher processing temperature (1200°C) used by the forced CVI process. Hot-face temperatures >1200°C were shown to cause significantly greater fiber degradation.

Silicon carbide matrix composites reinforced with Tyranno fibers were also fabricated by the forced CVI process. The room-temperature flexure strength of the material is at least as high as Nicalon-containing composites of similar density with similar strain tolerance. Improvement is noticeable in the strength of the Tyranno-reinforced composites over that of Nicalon-reinforced composites tested at temperatures up to 1200°C. The dependence of the strength of Nicalon-reinforced composites on processing temperature will provide an impetus to further investigate Tyranno fibers.

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