2/19-90 JS①

ORNL/TM-11524

OAK RIDGE NATIONAL LABORATORY

MARTIN MARIETTA

Mechanical Property Characterization of Fiber-Reinforced SiC Matrix Composites

D. P. Stinton
R. A. Lowden
R. H. Krabill

Fossil
Energy
Program

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 626-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.
NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DO NOT MICROFILM
THIS PAGE

ORNL/TM--11524

DE90 010257

Metals and Ceramics Division

MECHANICAL PROPERTY CHARACTERIZATION OF FIBER-REINFORCED SiC MATRIX COMPOSITES

D. P. Stinton, R. A. Lowden, and R. H. Krabill

Date Published: April 1990

NOTICE: This document contains information of a preliminary nature. It is subject to revision or correction and therefore does not represent a final report.

Prepared for the
U.S. DOE Fossil Energy AR&TD Materials Program
AA 15 10 10 0

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831-6285
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under contract DE-AC05-84OR21400

EB

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

MECHANICAL PROPERTY CHARACTERIZATION OF FIBER-REINFORCED SiC MATRIX COMPOSITES*

D. P. Stinton, R. A. Lowden, and R. H. Krabill

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. Flexure strengths, tensile strengths, and fracture toughnesses measured at room temperature and flexure strengths measured at high temperatures are nearly identical for composites fabricated by the two processes provided that hot-face temperatures <1200°C are used for the forced CVI process. Reduced strengths are observed for composites fabricated by forced CVI at temperatures >1200°C because of the degradation in strength of Nicalon fibers. Composites reinforced with more stable Tyranno fibers were fabricated by forced CVI and exhibited mechanical properties similar to those of Nicalon-reinforced composites. Composites reinforced with Tyranno fibers also exhibited 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.

---

*Research sponsored by the U.S. Department of Energy, Fossil Energy AR&TD Materials Program [DOE/FE AA 15 10 10 0, Work Breakdown Structure Element ORNL-1(A)] under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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) in St. Medard en Jalles, France, 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,

ORNL-DWG 89-17017

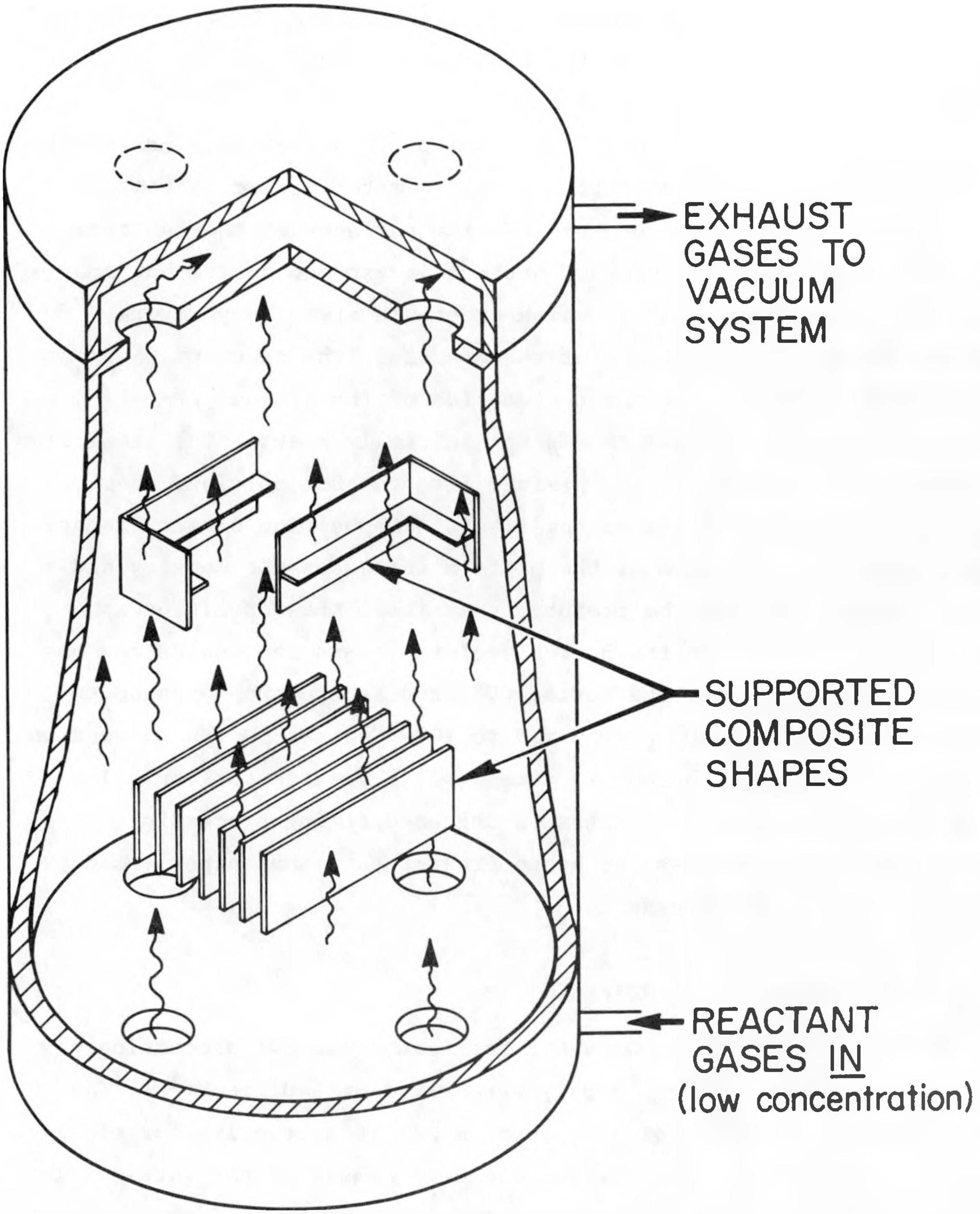

Fig. 1. **Schematic representation of the isothermal CVI process.** Reactant gases, as they flow through the furnace at a reduced pressure, diffuse into fibrous preforms and effluents diffuse back to the preform surface.

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[4-8] 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 (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). Again, the strength of the fibers is degraded during processing; however, the strength loss may be no greater than that experienced by the conventional CVI process.

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.[9-10] 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.[11-12] The implication

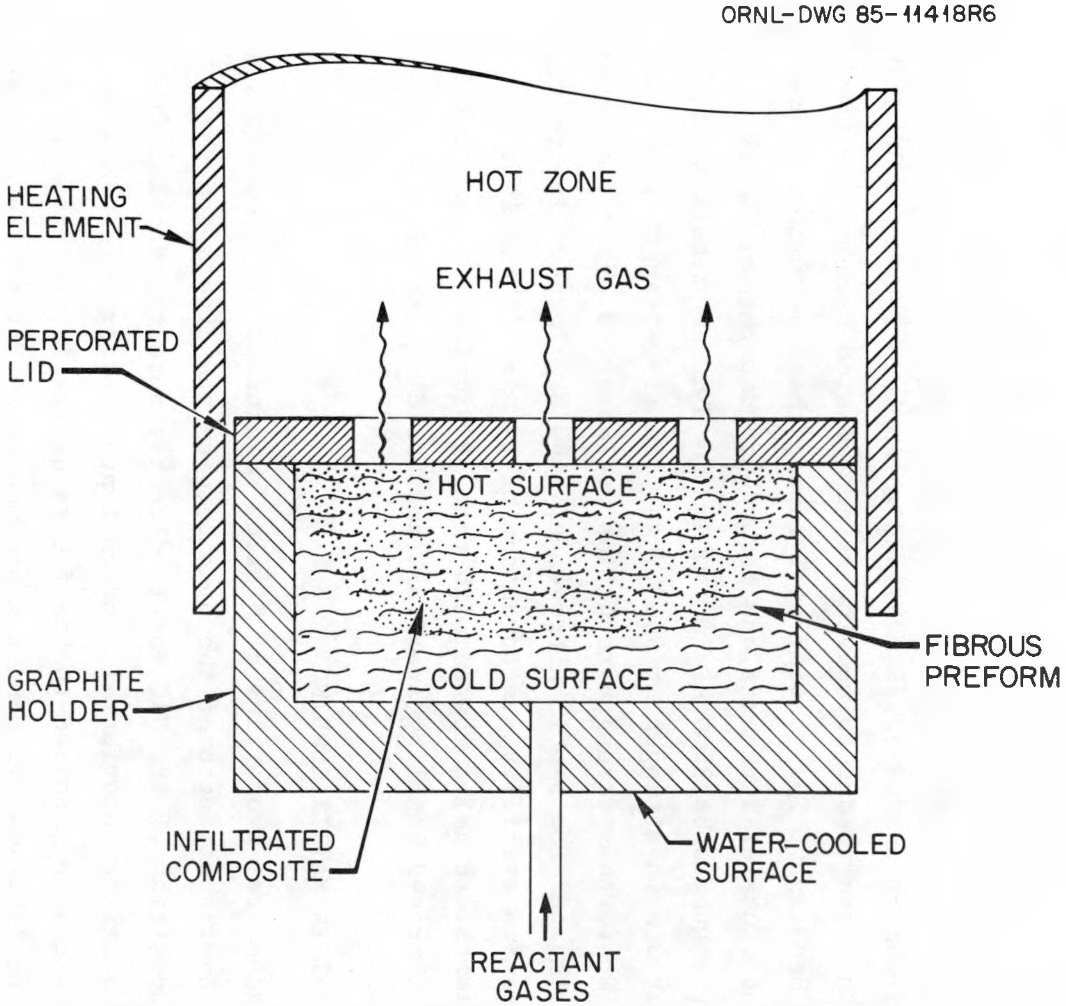

Fig. 2. Schematic representation of the forced flow-thermal gradient CVI process. Reactant gases are forced under pressure into the cooled side of the fibrous preform and flow toward the hot side, where SiC is readily deposited on the fibers.

is that exposure to elevated temperatures during processing or in service may have a detrimental effect on the strengths of infiltrated composites.

As a result of the reported higher stability of Tyranno over Nicalon, Tyranno reinforcing fibers are of great interest (Table 1).[13] Nippon Carbon Company reported the strengths of Nicalon to be 2900 MPa; however, lower strengths (2315 MPa) were measured on fiber tows received at ORNL. Further strength reduction was observed after the Nicalon fibers were carbon coated (2175 MPa) and woven into fabric (1730 MPa). Reduction in strength due to weaving is anticipated because the tows are damaged by handling. Tow testing of Tyranno fibers performed at the National Institute of Standards and Technology determined the as-received strength to be 3500 MPa.[14] After the Tyranno fibers were annealed for 3 h in nitrogen at 900°C, the tensile strength decreased to 2000 MPa. No further strength reduction was observed after the Tyranno fibers were heated for 3 h in nitrogen at 1400°C. In addition to their high-temperature stability, an advantage of Tyranno fibers is their smaller diameter (8 μm) compared with that of Nicalon (15 μm), which results in improved handling, weaving, and braiding behavior.

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.[14-18]

Table 1. Properties of Nicalon and Tyranno fiber reinforcements

Fiber	Treatment/condition	Tensile strength (MPa)	Tensile modulus (GPa)
Nicalon[a]	Manufacturer's data	2900 ± 395	195 ± 15
	As received[b]	2315 ± 160	
	Carbon coated[b]	2175 ± 191	
	From fabric[b]	1730 ± 126	
	1200°C in argon[c]	1234	108
	1200°C in air[c]	660	110
	1 h, 1200°C, 10% HCl/H_2[b]	861 ± 70	
	25 h, 1200°C, 10% HCl/H_2[b]	71 ± 15	
Tyranno[d]	As received[e]	3500	200
	3 h, 900°C, N_2[e]	2000	
	3 h, 1400°C, N_2[e]	2000	

[a] Nippon Carbon, Tokyo.

[b] Testing of fiber tows performed at Oak Ridge National Laboratory. *Source*: R. A. Lowden, *Characterization and Control of the Fiber-Matrix Interface in Fiber-Reinforced Ceramic Composites*, ORNL/TM-11039, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 1989.

[c] *Source:* T. Mah et al., "Thermal Stability of SiC (Nicalon)," *J. Mater. Sci.* 19, 1191-201 (1984).

[d] UBE Industries, Tokyo.

[e] Testing of fiber tows at The National Institute of Standards and Technology. *Source:* B. A. Bender, J. S. Wallace, and D. J. Schrode, "Effects of Thermochemical Treatments on the Strength and Microstructure of SiC Fibers," *J. Mater. Sci.*, accepted for publication.

The usefulness of the pyrolytic carbon is, however, limited by its low resistance to oxidation. Boron nitride has greater resistance to oxidation and can be used to slightly higher temperatures,[19] as demonstrated in Fig. 3. Also, boron doping of pyrolytic graphite improves its oxidation resistance (Fig. 3).

ORNL-DWG 89M-18988A

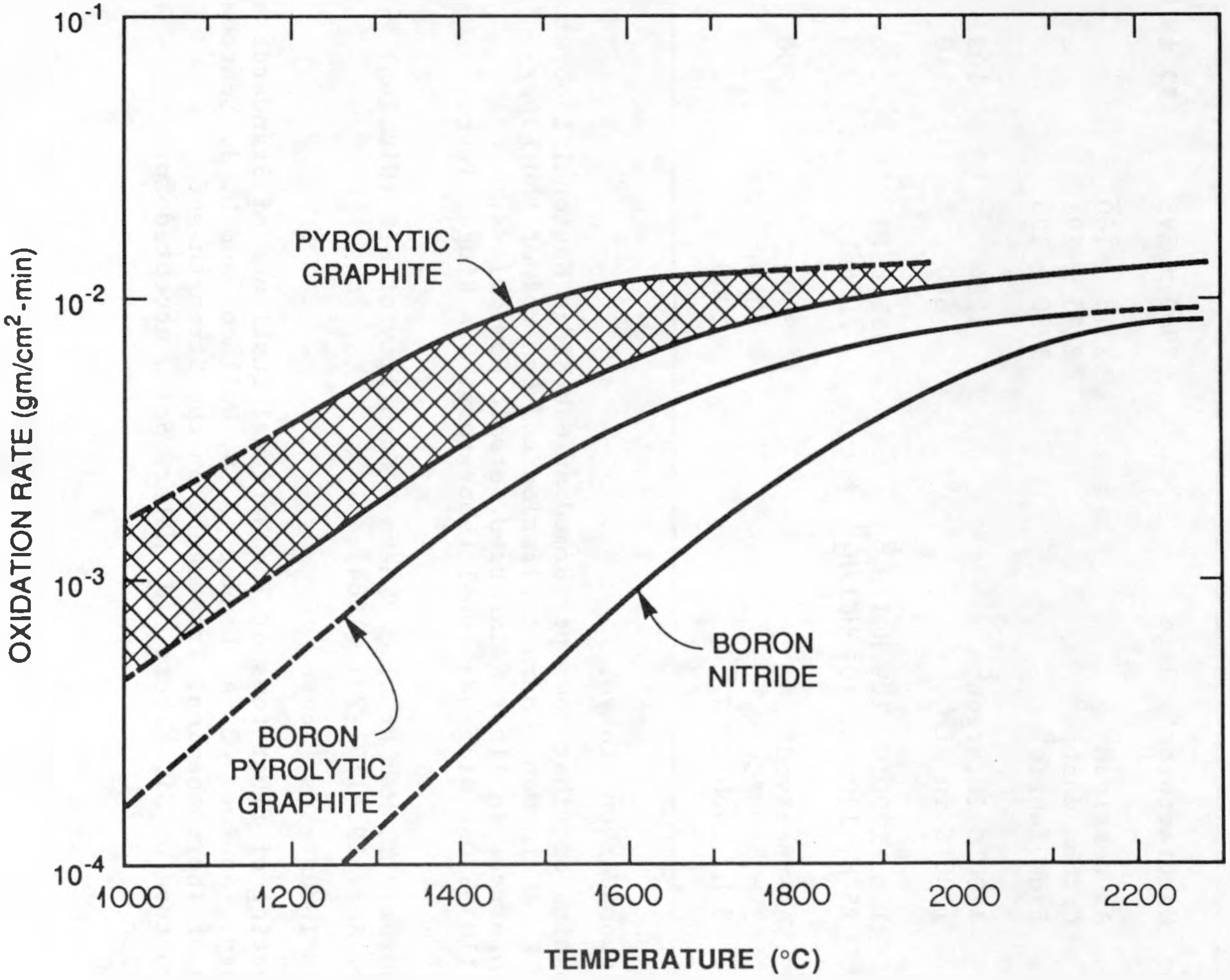

Fig. 3. Oxidation comparison of pyrolytic graphite, boron-doped pyrolytic graphite, and boron nitride. Boron nitride offers improved oxidation resistance when compared with pyrolytic graphite. *Source:* Based on data with permission from W. C. Riley, "Graphite," pp. 62-64 in *Ceramics for Advanced Technologies*, ed. J. E. Hove and W. C. Riley, Wiley, New York, 1965.

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° ± 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 pinned to the holder. The cloth sizing was removed through multiple washings with acetone. Two sizes of fibrous preforms were constructed, small disks (45 mm in diameter, 12.5 mm thick) and larger disks (75 mm diameter, 16 mm thick).

After assembly, preforms were precoated with thin layers of carbon. The coatings were deposited from an argon/propylene mixture at 1100°C and 3.3 kPa for 2 h. The thickness of the carbon interlayer, 0.2 to 0.3 μm, was verified by polarized-light optical microscopy of metallographic cross sections. Boron nitride coatings were applied instead of carbon to a few 45-mm-diam preforms. For these preforms, Nicalon fabric was coated with boron nitride (BN) by the Chemical Vapor Deposition Department of Comhurex, Pierrelatte, France. Boron nitride layers 0.2 to 0.3 μm thick were deposited on plain-weave cloth from a mixture of boron trichloride, ammonia, and hydrogen under proprietary processing conditions. Fibrous preforms were assembled from the BN-coated cloth as previously described.

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 2. Note that the processing times decreased from about 36 h for a top temperature of 1100°C to only 9 h for a top temperature of 1400°C.

Table 2. 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.

The processing times are not always linear (e.g., run 353 was longer than anticipated), because graphite seals within the furnace sometimes leak and allow reactant gases to bypass the composite specimen.

A second series of composite specimens was fabricated for our investigation of the effect of elevated temperatures on the mechanical properties of the composite material. The processing conditions from these composites are described in Table 3. The configuration of the equipment when these specimens were fabricated resulted in a bottom temperature about 100°C lower than that of the smaller furnace, which failed to fully infiltrate the bottom layers of the composite. The hot-face temperatures for these specimens was increased to 1270°C to increase the bottom temperature. After fabrication of these composites, a recirculator was developed that yields better control of the bottom temperature of the part.

A third series of composites was fabricated from Tyranno fabric to determine the room-temperature mechanical properties. The processing conditions for these runs are described in Table 4.

Table 3. Composites fabricated for investigation of elevated temperature flexural strengths (All samples were 75 mm diam, 16 mm thick, and fabricated at a hot-face temperature of 1270°C)

Run	Fiber type	Interface	Processing time (h)
255	Nicalon	Carbon	14.3
268	Nicalon	BN	34.0[a]
258	Tyranno	Carbon	14.1

[a] A faulty seal within the furnace allowed reactant gases to bypass the composite. After 24 h, the leak became apparent and the furnace was shut down. After installation of a proper seal, densification was completed in only 10 additional hours.

Table 4. Composites fabricated to investigate the mechanical properties of Tyranno-reinforced material

Run	Fiber content (%)	Sample diameter (mm)	Processing temperature (°C)	Processing time (h)
242	43	45	1200	12.5
243	43	45	1200	38.1
269	40	45	1200	21.1

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. All specimens were measured and weighed to determine densities.

Room-temperature flexural strengths were determined from linear elastic-beam assumptions and the maximum load 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. The larger bend bars were used for elevated-temperature flexure testing. The specimens 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 from linear elastic-beam assumptions and the maximum load by four-point bending, with a support span of 40 mm, a loading span of 20 mm, and a loading rate of 1.0 kg/s (crosshead speed of 0.0075 to 0.011 mm/s). The tests were performed with alumina fixtures at 25, 500, 750, 1000, and 1200°C. 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); fracture toughness values were calculated from the maximum loads and the stress-intensity-factor coefficients from Brown and Srawley for linear elastic behavior.

RESULTS AND DISCUSSION

Room-temperature flexure strengths have been measured on composites fabricated by the forced CVI process for several years.[20] 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).[20]

These values are nearly identical to those reported by Lamicq et al.[21] for Nicalon-reinforced SiC matrix composites infiltrated at SEP by the isothermal CVI process.

Minor improvements to the forced CVI process were made to increase average flexure strengths of the typical composite to about 380 MPa. Mechanical properties of several typical samples are described in Table 5. 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 strength. When large numbers of samples were examined in a previous study,[20] strength was related to density but significant scatter in the data indicated that other factors also affect strength.

Table 5. **Characterization of Nicalon-reinforced composites**

Sample	Fiber content (vol %)	Sample location	Composite density (% theorotical)	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

As other researchers have reported,[22-26] the tensile strength of ceramics is difficult to precisely measure. All the difficulties associated with precision tensile testing (e.g., alignment of top and bottom grip centerlines, alignment of sample centerline to grip centerline, precision sample machining) are magnified by the brittle nature of ceramics. The short length of the samples fabricated at ORNL resulted in a short gage length (13 mm), which magnified the stresses that any misalignment would place on the samples. The short sample length also resulted in a minimum length (16 mm) available for bonding of the samples to the grips. Because these tests are so time-consuming, few samples have been tested.

Successful tensile results were obtained by using the precision tensile-testing apparatus developed under the U.S. Department of Energy Advanced Materials Development Program by K. C. Liu et al.[24] Liu's testing of this equipment indicated that bending stresses at a specimen length of 140 mm were <0.5% of the applied tensile stress. To accommodate the shorter samples, precision-machined metal adapters were used in conjunction with a sample-grip system. Similar stress-strain curves from strain gages mounted on the front and back surfaces of the tensile sample indicated that the sample was properly aligned with the testing machine. A typical strain-gage-derived stress-strain curve for the fiber-reinforced composites [85% of theoretical density (T.D.)] is shown in Fig. 4. Note that at the maximum load, the stress is ~230 MPa and the strain is ~0.75%. Both values are comparable to values reported by Lamicq et al.[21] for similar material fabricated by the isothermal CVI process.

Apparent fracture toughness measured for composites fabricated from Nicalon cloth by the forced CVI process is 23.5 ± 2.9 MPa•m$^{1/2}$, which is nearly identical to the room-temperature value reported by Du Pont or SEP[20] (25 MPa•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. The cloth used by SEP and Du Pont is a plain weave with 500 filaments/tow and about 10 tows/cm, whereas the cloth used at ORNL is also plain weave but contains 1000 filaments/tow and only about 6 tows/cm. The more open weave of the cloth used at ORNL seems to provide better movement of reactants through the preform, which is beneficial to the forced CVI process.

ORNL-DWG 86-11226

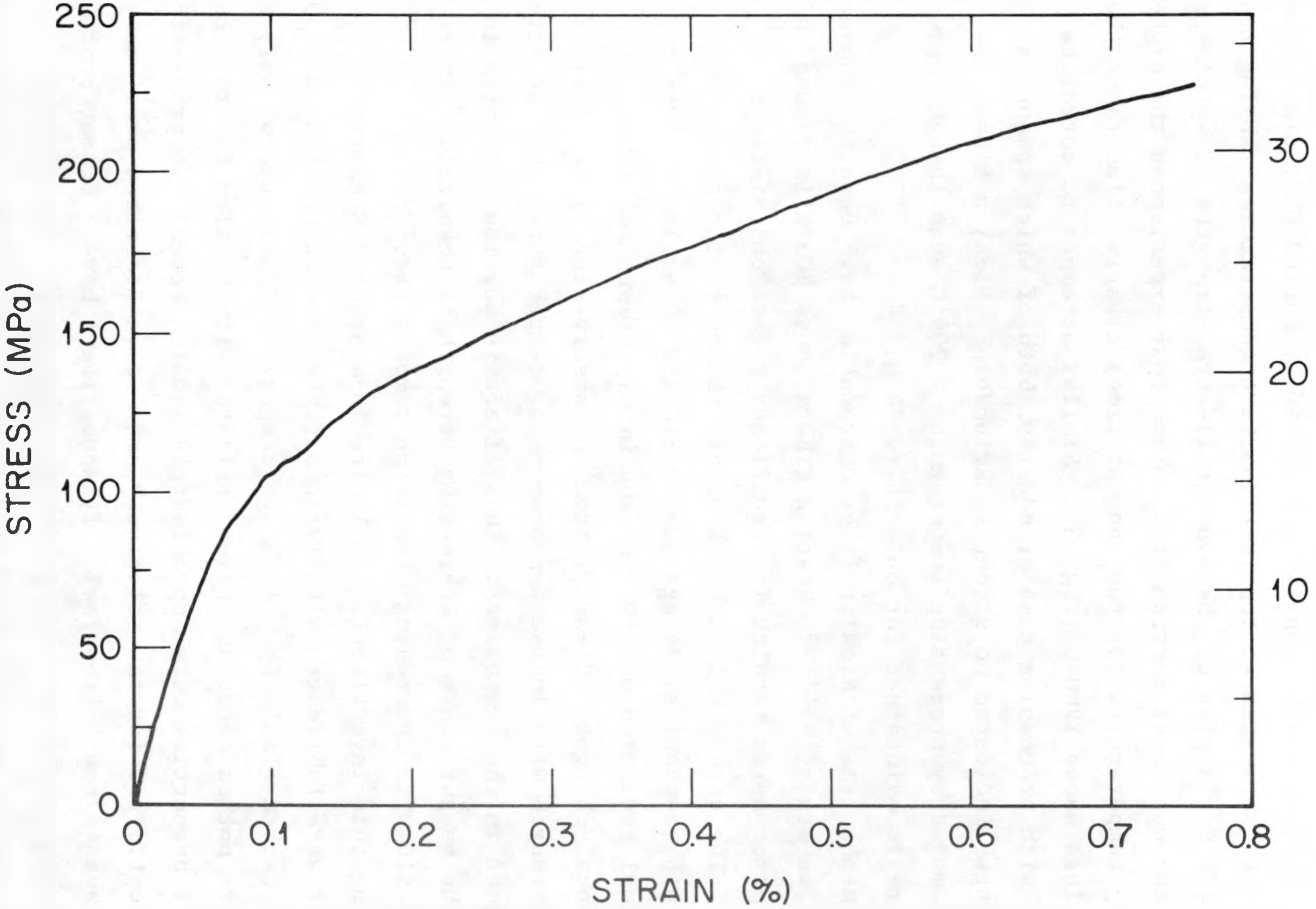

Fig. 4. Strain-gage-derived tensile-stress-strain curve for a typical Nicalon-reinforced SiC matrix composite (~40% fiber) fabricated by forced CVI processing.

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 1000 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. 5). Similar attempts to correlate strengths with processing time or density, both of which spanned a narrow range, indicated no strong relationship. Nicalon fibers are clearly damaged by processing temperatures >1200°C even though the temperature is maintained for only 16 to 24 h.

The mechanisms of Nicalon-fiber degradation have been the subject of extensive study.[11,12,27-29] Heating fibers above 800°C in vacuum, air, or inert atmospheres results in significant reductions of fiber strength. The strength loss has been attributed to factors such as grain growth, mechanical damage due to SiO and CO evolution from the carbothermal reduction of SiO_2 present in the fiber, and other compositional changes. Clearly, from the observation of decreasing flexure strength with increasing processing temperature, such an effect is confirmed in the composites. This effect is particularly true in view of the measurements of increasing strength of chemically vapor deposited SiC with increasing deposition temperature.[30-33]

During this investigation, a limited number of SiC-matrix composites were fabricated with Tyranno fibers precoated with ~0.2 μm of pyrolytic carbon (Table 6). 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 described previously (1000 filaments/tow, 6 tows/cm). Tyranno fibers have a diameter of 8 to 10 μm and are available in only 1000-filament tows. The smaller diameter flexible fibers form a tight bundle with little porosity, which makes them difficult to infiltrate. The forced CVI process needs to be optimized for the tightly woven Nicalon and the more nested Tyranno

ORNL-DWG 90-9543

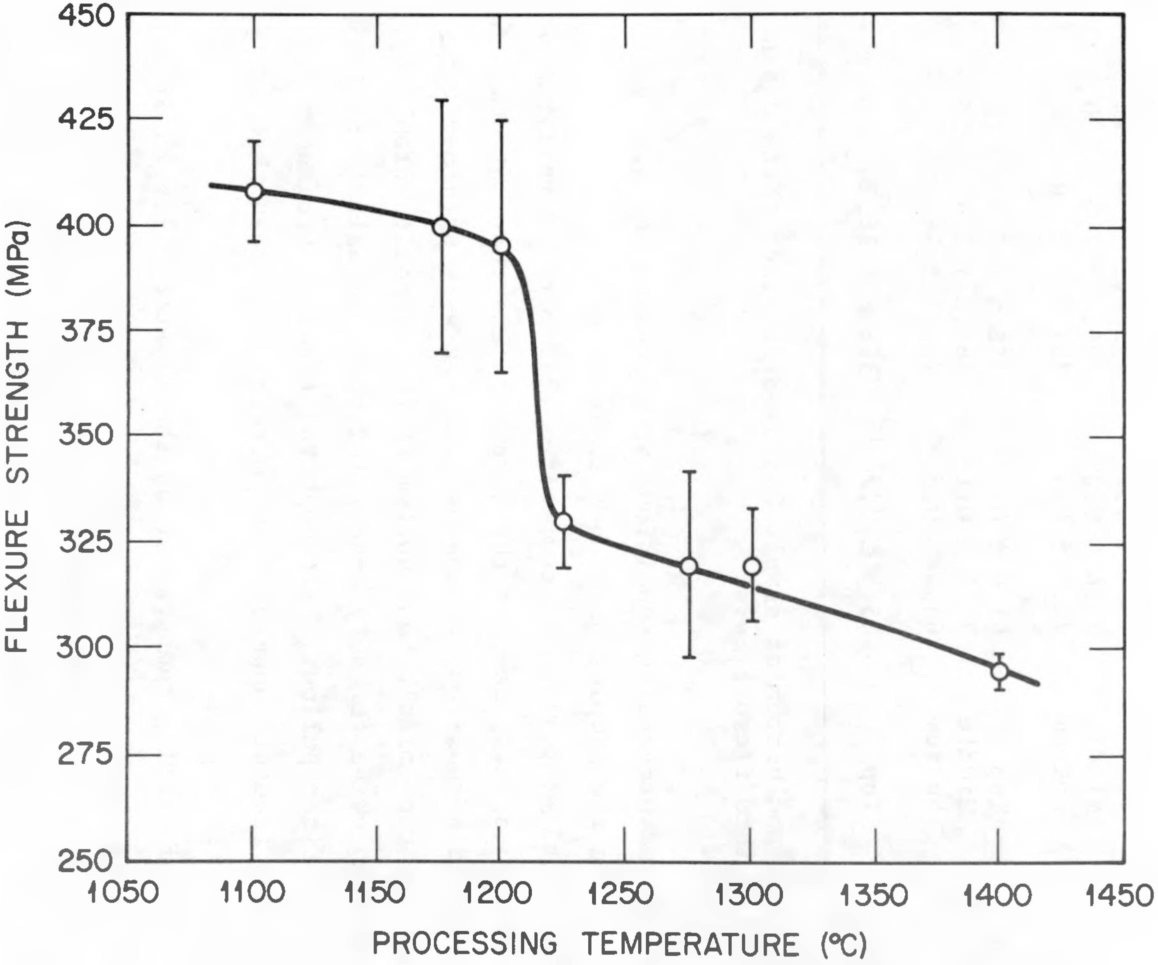

Fig. 5. Correlation of room-temperature flexure strength with processing temperature as measured on the hot face of the Nicalon-reinforced SiC matrix composite.

Table 6. Characterization of composites reinforced with Tyranno fibers

Sample	Fiber content (vol %)	Sample location	Composite density (% theoretical)	Flexure strength (MPa)	Apparent fracture toughness (MPa•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 did not require cutting into flexure bars.

cloth. (Optimized processing conditions would reduce the wide variation in density within the samples described in Table 6.)

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 6). A load-displacement curve for a Tyranno-reinforced composite exhibits "toughening" by fiber pullout. Although the fracture toughness values are similar, the fracture appears to be more brittle than that of Nicalon composites (Fig. 6).

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. 7. A gradual increase in the strength of the Nicalon/SiC composites produced by forced CVI was observed up to a temperature of 1000°C. The same increase was observed for composites fabricated with either a carbon or boron nitride interface. The composites exhibited good strengths and gradual failure in all tests. A decrease in the strength

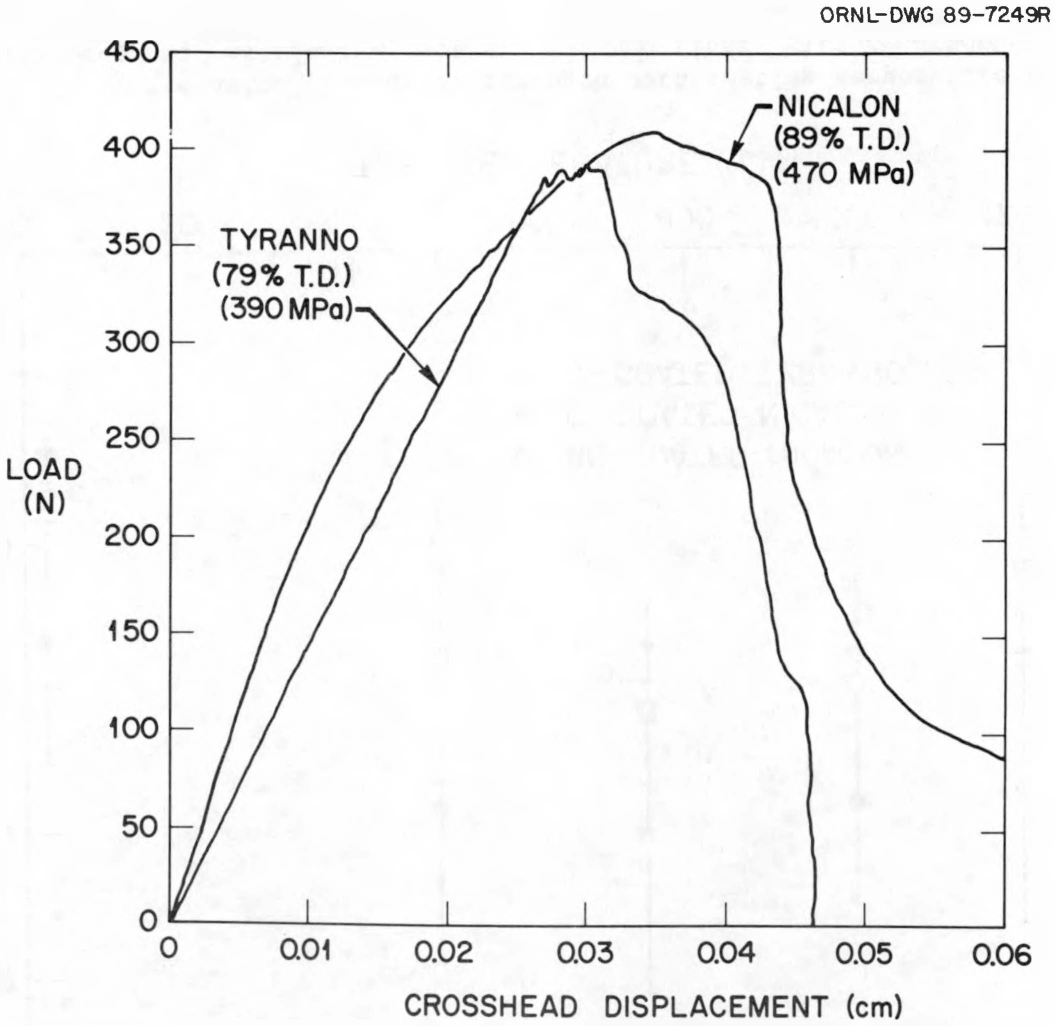

Fig. 6. Load displacement curves for Tyranno and Nicalon fiber-reinforced SiC matrix composites (four-point flexure bars). (T.D. = theoretical density.)

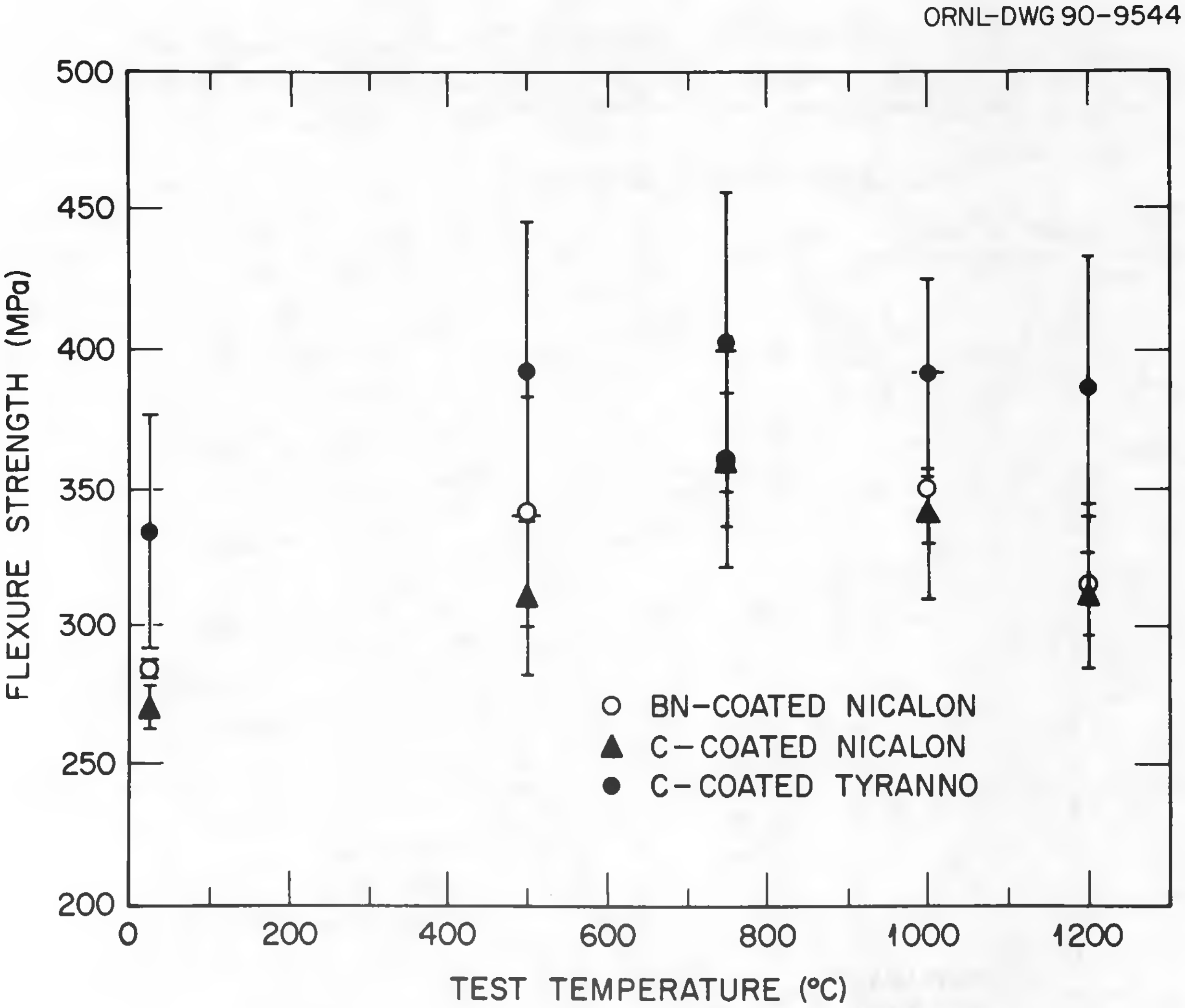

Fig. 7. Correlation of flexure strength with testing temperature for fiber-reinforced SiC matrix composites. Tyranno fibers with a carbon interface exhibit higher strengths at all temperatures than do Nicalon fibers with carbon or boron nitride interfaces.

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.[21] 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 tensile strength, room-temperature fracture toughness, and high-temperature flexure strength. Forced CVI composites fabricated at hot-face temperatures $\leq$1200°C exhibit an average flexure strength of ~380 MPa and an apparent fracture toughness of ~23 $\mathrm{MPa \bullet m^{1/2}}$. Room-temperature tensile strengths obtained on a limited number of samples gave values of ~230 MPa. 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. The higher temperature stability of the Tyranno fibers could provide greater flexibility for the forced CVI process.

Plain-weave Nicalon cloth, used almost exclusively for the development of the forced CVI process, has a relatively open weave that permits movement of reactants through the thickness of the preform. The initial attempts to infiltrate more tightly woven Nicalon cloth similar to that used by SEP and Du Pont resulted in slightly lower densities. Current processing conditions do not permit sufficient time for a thorough infiltration of the fiber bundles that results in the lower densities. The forced CVI processing conditions must be optimized for the weave to increase the final density of the composite. Tyranno fibers are smaller in diameter and come in bundles of more filaments. Because these fibers nest together more tightly than do the stiffer Nicalon fibers, less permeability exists within the Tyranno bundles. Minor adjustments are needed for the forced CVI processing conditions to extend the infiltration time or other such modifications for more complete infiltration and uniformity improvement of the Tyranno-reinforced composites.

ACKNOWLEDGMENTS

The authors are indebted to M. K. Ferber and M. G. Jenkins, whose interest and valuable suggestions helped carry this work to completion. Their help is also greatly appreciated for instruction and assistance in making mechanical property measurements on High Temperature Materials Laboratory equipment. The authors are grateful for the assistance of L. Riester, H. R. Livesey, and C. A. Valentine for preform assembly, drawing preparation, and draft manuscript preparation, respectively, and H. D. Neu for final manuscript preparation.

REFERENCES

1. F. Christin et al., "In-Depth Chemical Vapor Deposition of SiC Within Porous Carbon-Carbon Materials," *Proc. 3rd European Conf. Chem. Vapor Dep.*, 154 (1980).

2. J. W. Warren, "Fiber- and Grain-Reinforced CVI Silicon Carbide Matrix Composites," *Ceram. Eng. Sci. Proc.* **6**(7-8), 64 (1985).

3. P. J. Lamicq et al., "SiC/SiC Composite Ceramics," *Ceram. Eng. Sci. Proc.* **6**(7-8), 336-38 (1985).

4. D. P. Stinton, A. J. Caputo, and R. A. Lowden, "Synthesis of Fiber-Reinforced SiC Composites by Chemical Vapor Infiltration," *Am. Ceram. Soc. Bull.* **65**(2), 347-50 (1986).

5. A. J. Caputo and W. J. Lackey, "Fabrication of Fiber-Reinforced Ceramic Composites by Chemical Vapor Infiltration," *Ceram. Eng. Sci. Proc.* **5**(7-8), 654-67 (1984).

6. D. P. Stinton, "Ceramic Composites by Chemical Vapor Infiltration," pp. 1028-40 in *Proc. Tenth Intl. Conf. Chem. Vapor Dep.*, ed. G. W. Cullen, Electrochemical Society, Pennington, N.J., 1987.

7. D. P. Stinton, T. M. Besmann, and R. A. Lowden, "Advanced Ceramics by Chemical Vapor Deposition Techniques," *Am. Ceram. Soc. Bull.* **67**(2), 350-55 (1988).

8. M. H. Headinger and M. J. Purdy, "Design of a Production-Scale Process for Coating Composite Structures," *Surf. Coat. Tech.* **33**, 433 (1987).

9. S. Yajima et al., "Systhesis of Continuous SiC Fibers with High Tensile Strength," *J. Am. Ceram. Soc.* **59**(7-8), 324-27 (1976).

10. S. Yajima et al., "Anomalous Characteristics of the Microcrystalline State of SiC Fibers," *Nature* **27**(21), 706-7 (1979).

11. T. Mah et al., "Thermal Stability of SiC (Nicalon)," *J. Mater. Sci.* **19**, 1191-201 (1984).

12. G. Simon and A. R. Bunsell, "Creep Behavior and Structural Characterization at High Temperatures of Nicalon SiC Fibers," *J. Mater. Sci.* **19**, 3658-70 (1984).

13. T. Yamamura et al., "Compatibility of New Continuous Si-Ti-C-O Fiber for Composites," pp. 19-28 in *Looking Ahead for Materials and Processes*, ed. J. deBossou, G. Briens, and P. Lissac, Elsevier, Amsterdam, 1987.

14. B. A. Bender, J. S. Wallace, and D. J. Schrode, "Effects of Thermochemical Treatments on the Strength and Microstructure of SiC Fibers," *J. Mater. Sci.*, accepted for publication.

15. R. A. Lowden, *Characterization and Control of the Fiber-Matrix Interface in Fiber-Reinforced Ceramic Composites,* ORNL/TM-11039, Oak Ridge National Laboratory, Oak Ridge, Tenn., March 1989.

16. R. W. Rice et al., "The Effect of Ceramic Fiber Coatings on the Room-Temperature Behavior of Ceramic-Fiber Composites," *Ceram. Eng. Sci. Proc.* **2**(7-8), 661-701 (1981).

17. B. Bender et al., "Effect of Fiber Coatings and Composite Processing of Properties of Zirconia-Based Matrix SiC Fiber Composites," *Am. Ceram. Soc. Bull.* **65**(2), 363-9 (1986).

18. A. J. Caputo, D. P. Stinton, R. A. Lowden, and T. M. Besmann, "Fiber-Reinforced SiC Composites with Improved Mechanical Properties," *Am. Ceram. Soc. Bull.* **66**(2), 268-72 (1987).

19. W. C. Riley, "Graphite," pp. 62-64 in *Ceramics for Advanced Technologies*, ed. J. E. Hove and W. C. Riley, Wiley, New York, 1965.

20. A. J. Caputo, D. P. Stinton, R. A. Lowden, and T. M. Besmann, "Fiber-Reinforced SiC Composites with Improved Mechanical Properties," *Am. Ceram. Soc. Bull.* **66**(2), 368-72 (1987).

21. P. J. Lamicq et al., "SiC/SiC Composite Ceramics," *Am. Ceram. Soc. Bull.* **65**(2), 336-38 (1986).

22. J. J. Mecholsky, "Evaluation of Mechanical Property Testing Methods for Ceramic Matrix Composites," *Am. Ceram. Soc. Bull.* **65**(2), 315-22 (1986).

23. D. Lewis et al., "Standardized Testing of Refractory Matrix/ Ceramic Fiber Composites," *Ceram. Eng. Sci. Proc.* 5(7-8), 507-23 (1984).

24. K. C. Liu and C. R. Brinkman, "Tensile Cyclic Fatigue of Structural Ceramics," pp. 279-84 in *Proceedings of the Twenty-Third Automotive Technology Development Contractors' Coordination Meeting*, Dearborn, Mich., Oct. 21-24, 1985, Soc. Automot. Eng., Warrendale, Pa., March 1986.

25. B. W. Christ and S. R. Swanson, "Alignment Problems in the Tensile Test," *J. Test. Eval.* 4(6), 405-17 (1976).

26. F. F. Lange and E. S. Diaz, "Powder-Cushion Gripping to Promote Good Alignment in Tensile Testing," *J. Test Eval.* **6**(5), 320-23 (1976).

27. T. J. Clark et al., "Thermal Stability Characterization of SiC Ceramic Fibers I, Mechanical Property and Chemical Structure Effects," *Ceram. Eng. Sci. Proc.* **7**(7-8), 901-13 (1986).

28. S. M. Johnson et al., "Degradation Mechanisms of Silicon Carbide Fibers," *J. Am. Ceram. Soc.* **71**(3), C132-5 (1988).

29. A. S. Fareed et al., "Thermomechanical Properties of SiC Yarn," *Am. Ceram. Soc. Bull.* **66**(2), 353-8 (1987).

30. J. A. Coppola and R. C. Bradt, "Measurement of Fracture Surface Energy of SiC," *J. Am. Ceram. Soc.* **55**(9), 455-60 (1972).

31. T. D. Gulden, "Mechanical Properties of Polycrystalline Beta-SiC," *J. Am. Ceram. Soc.* 5(11), 585-90 (1969).

32. R. J. Price, "Structure and Properties of Pyrolytic Silicon Carbide," *Am. Ceram. Soc. Bull.* **48**(9), 859-62 (1969).

33. D. P. Stinton and W. J. Lackey, "Effect of Deposition Conditions on the Properties of Pyrolytic SiC Coatings for HTGR Fuel Particles," *Am. Ceram. Soc. Bull.* **57**(6), 568-73 (1978).