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Improvements in the Fabrication of Ceramic-Fiber–Ceramic-Matrix Composites by Chemical Vapor Infiltration

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METALS AND CERAMICS DIVISION

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IMPROVEMENTS IN THE FABRICATION OF CERAMIC-FIBER–CERAMIC-MATRIX COMPOSITES BY CHEMICAL VAPOR INFILTRATION*

A. J. Caputo, R. A. Lowden, and D. P. Stinton

ABSTRACT

Development of a new, faster process for the fabrication of ceramic-fiber-reinforced–ceramic-matrix composites by chemical vapor infiltration has continued. Composites of SiC fibers infiltrated with a matrix of either SiC or Si_3N_4 have been produced. Process and equipment improvements led to the fabrication of preforms with a higher fiber content, and infiltration improvements reduced infiltration times and increased infiltrated densities. These improvements have produced composites with higher flexural strengths (up to 475 MPa) and high strain values (up to 1%). The high strength and high strain values along with the gradual loss of strength (in contrast to the sudden loss typical of ceramics) were major goals of this work.

INTRODUCTION

Ceramic-fiber–ceramic-matrix composites are receiving significant attention because of their potential for improved toughness and strength while retaining the normal ceramic attributes of refractoriness and resistance to abrasion and corrosion. In recent years, high toughness and strength values have been reported for various fiber-reinforced ceramic composite systems.[1-4] However, conventional ceramic fabrication processes can thermally, mechanically, or chemically damage the fibers during green-state formation and sintering of the composite. For example, the fibers may be broken during pressing, or they may react chemically with the matrix or otherwise be changed during high-temperature processing. The objective of this work was to synthesize composites by fabricating ceramic-fiber preforms and then forming the ceramic matrix by infiltration with a practical, low-stress, low-temperature, chemical vapor deposition (CVD) process.

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Other workers have utilized CVD to form the matrix of fiber-reinforced ceramic composites.[5-14] The earliest work employed carbon fibers and a carbon matrix, but later work included matrices of SiC, Si_3N_4, BN, and TiB_2. Such composites have excellent mechanical properties, but, without exception, processing times required for CVD infiltration have been extremely long (several weeks). Thermodynamic and kinetic considerations that address these long infiltration times have been reported previously.[15-19] Our goal was to reduce processing times to a matter of hours so that composite costs could be reduced sufficiently to make these materials economically practical for engineering applications.

EXPERIMENTAL PROCEDURE

EQUIPMENT DEVELOPMENT

The CVD infiltration method used in this work is a new approach combining thermal-gradient and pressure-gradient processes.* Initial work with the process was reported previously,[20-24] and continued development of the process is discussed in this report. A schematic of the critical portion of the equipment, the gas injector and preform holder, is shown in Fig. 1. Initially, the fibrous preform was positioned in the cavity within the water-cooled metal holder. The metal holder cooled the bottom and side surfaces of the preform to prevent deposition of matrix material at those locations. The top of the preform was heated by the furnace. This approach provided substantial cooling but produced a relatively small specimen: 25 mm (1 in.) in diam by 6 mm (0.25 in.) thick.

After the initial studies, it was apparent that the process would operate properly with considerably less cooling. Therefore, a graphite holder was placed on top of the water-cooled metal holder as shown in Fig. 1. The graphite holder was cooled sufficiently by contacting the water-cooled metal holder to prevent deposition on the bottom and side surfaces of the preform. Cooling the graphite holder only from the bottom provided sufficient space to increase the preform size to 50 mm (2 in.)

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*Patent pending.

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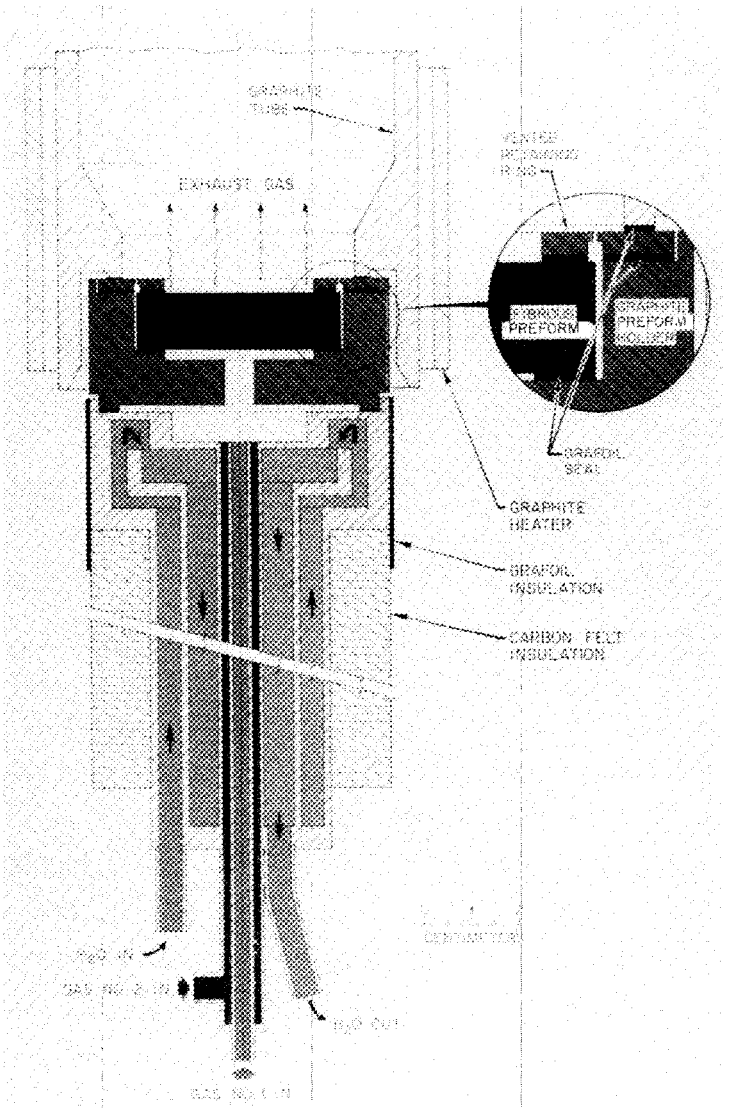

Fig. 1. Water-cooled gas injector and preform holder is the key equipment item for a modified chemical vapor deposition system for infiltration of fiber-reinforced ceramic composites.

in diam by 12 mm (0.5 in.) thick. Reactant gases pass through the water-cooled gas injector and through the cooler regions of the preform but deposit as dense matrix material within the hotter regions near the top of the preform. Initially, the gases are able to flow both axially and radially through the preform. However, when the top surface becomes

coated, the gases must flow radially through the preform to the annular void around the preform and escape through the holes in the retaining ring. As a result, the fibers in the preform are coated uniformly, thus forming the matrix phase of the composite. As the matrix is deposited, the thermal conductivity of the infiltrated portions of the preform increases and the deposition zone progressively moves from the top of the preform toward the bottom and the circumference.

Flexibility of this new process was demonstrated by the infiltration of tubular preforms to a density of about 85%. This is an important advance because the ability to fabricate tubes or hollow cylinders demonstrates the potential for the process to be used for fabrication of toughened high-strength heat exchanger tubes and heat engine cylinder liners or valve guides.

Another advantage of the new process was apparent when a change in the gas flow sequence resulted in faster deposition rates and shorter infiltration times. First the preform was loaded into the furnace with a retaining ring that had no vent holes. This forced *all* the gases to flow through the preform and therefore increased the deposition rate. After several hours of deposition, gases could no longer pass through the top surface and back pressure increased within the furnace. The run was stopped, and the retaining ring without holes was removed and replaced with a ring containing holes. The deposition was restarted with the gases flowing into and radially through the preform and exiting through the holes in the retaining ring. Deposition continued until the bulk of the porosity was infiltrated as indicated by an increase in back pressure.

PREFORM FABRICATION

Slurry molding (also called vacuum forming) was used to fabricate some of the fibrous preform disks (50 mm in diam by 12 mm thick) infiltrated in this research. Most of our work used NICALON* SiC fibers, although some work was performed with SILAR† or Tokamax‡ SiC fibers. In the slurry

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*Nippon Carbon Company, Tokyo, Japan.

†Arco Chemical, Greer, S.C.

‡Tokai Carbon Company, Tokyo, Japan.

molding process, chopped fibers are first suspended in a liquid containing polycarbosilane binder. The slurry is then vacuum filtered to form a disk. A more detailed description of the procedure used for preparation of preforms was reported previously.[20-23]

Higher density preforms were fabricated by stacking layers of NICALON SiC cloth (orthogonal weave, two dimensional) or by using aligned fiber arrays (unidirectional reinforcing) cut from a spool of continuous NICALON fibers.

Two types of SiC cloth, plain and satin weave, were used to form the cloth-reinforced parts. The cloths have the same basic properties, varying only in the weave characteristics as shown in Fig. 2. The cloth was cut into 45-mm-diam pieces, and a 12-mm-thick disk was formed by stacking layers of cloth in a graphite holder. The cloth layers were stacked with either a 0-30-60-90° or 0-90° orientation between layers.

To form the unidirectionally reinforced parts, continuous fibers were wound around pins spaced about 30 cm apart. Pieces 25 mm long were cut from the resulting tape (~25 mm wide), and the part was formed by stacking layers of unidirectional lengths in a graphite holder. A graphite lid with multiple holes to permit passage of the CVD gas was used to compress the layers and hold them in place. The entire graphite holder was ultrasonically cleaned with acetone before CVD infiltration.

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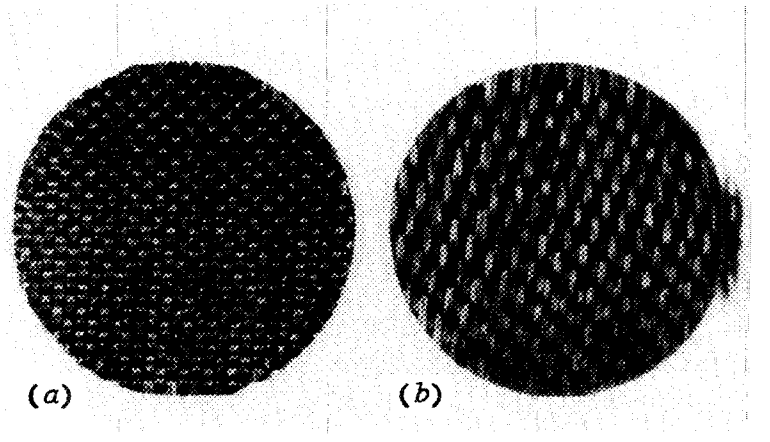

Fig. 2. NICALON SiC cloth. (*a*) Plain weave. (*b*) Satin weave.

CVD INFILTRATION

Most of this work investigated the infiltration of SiC fibers with CVD SiC, although infiltration of SiC fibers with Si_3N_4 was also examined. The Si_3N_4 was deposited by using $SiCl_4$, NH_3, and H_2; the SiC was deposited by using CH_3Cl_3Si and H_2. Because NH_3 and $SiCl_4$ react to form ammonium chlorides at low temperatures, the inlet gas flows during Si_3N_4 deposition were kept separated until the gases entered the deposition region (Fig. 1). Deposition of SiC requires only one inlet line because no low-temperature reactions occur between CH_3Cl_3Si and H_2.

The influence of various parameters on composite properties was investigated during previous studies of the SiC and Si_3N_4 deposition processes. Process parameters continue to be investigated and reported,[21-28] and composites are being infiltrated at 1200°C and at pressures between 3 and 100 MPa (20 to 760 torr). Deposition at higher temperatures is precluded by fiber damage and resultant strength reduction.

MECHANICAL PROPERTIES

Flexural strength data were obtained at room temperature, on various composites synthesized under various process conditions, by using four-point flexure. Samples were taken from the top, middle, and bottom of each composite specimen. The highest densities were produced at the top of the specimen (hot face during infiltration). Somewhat lower densities were produced at the middle, and considerably lower densities were produced at the bottom (cold face during infiltration). Although it was anticipated that higher strengths would be characteristic of the higher density composites, that was not always the case.

RESULTS AND DISCUSSION

FABRICATION OF PREFORMS

Initially, vacuum molding of chopped fibers resulted in the formation of preforms with a fiber content of about 15 vol % [15% of theoretical density (T.D.)]. Continued development increased this to a maximum of about

25 vol %. In an attempt to further increase the fiber volume fraction, preforms were prepared by vacuum molding followed by pressing in dies or between plates to a predetermined thickness. Although an occasional acceptable preform was produced with a fiber content of about 40% T.D., most pressings resulted in unacceptable parts that were not well bonded, that expanded when the pressure was released, or that expanded during one of the various heating cycles.

Preforms with higher fiber contents were fabricated by stacking layers of unidirectional fibers or woven cloth (two-dimensional fibers). The major problem with fabricating preforms from multiple layers of cloth is keeping the layers well bonded throughout the process steps. Initially we attempted to use a binder to hold the layers together until the infiltration step. This was unsuccessful because the parts tended to debond during processing (forming, drying, curing, heat treating, and infiltrating). However, the use of a binder appeared to be unnecessary if the part could be held in place without disturbance throughout processing. (The CVD matrix bonds the layers and prevents delamination.) Thus, a binder was used only to stiffen the cloth and prevent fraying and deweaving while the cloth was cut into circular pieces. After stacking the layers in a graphite holder and compressing them with the graphite lid, the assembly was ultrasonically cleaned to remove any sizing or binder. Cloth preforms containing 40 to 45 vol % fibers were fabricated routinely.

Preforms fabricated by essentially the same procedure and with unidirectional fibers had fiber contents in the range of 39 to 58 vol %. Preforms of the highest fiber content created such high back pressures that the flows had to be reduced by a factor of 5 to prevent leakage from the coating chamber. The decreased flows reduced the deposition rate and increased the infiltration time by about 50%. Preforms containing 45 vol % fibers reduced the flows by a factor of 2. After some equipment modifications reduced leakage from the coating chamber, unidirectional preforms with 40 to 45 vol % fibers were infiltrated by using the normal flows.

SiC FIBERS, Si_3N_4 MATRIX

The flow rates of $SiCl_4$, NH_3, and H_2 have been varied in search of deposition conditions that produce a dense Si_3N_4 matrix and that minimize the formation of unstable compounds in the effluent lines.

Preforms containing 15 vol % chopped fibers were infiltrated to densities in the range of 1.6 to 2.1 Mg/m^3 (50 to 65% T.D.). Room-temperature flexural strength data for the specimens were obtained by four-point flexure. The strengths ranged from 37 to 62 MPa (5400 to 9000 psi) with the higher density specimens generally having the higher strengths. Although these values are considerably lower than desired, some of the specimens exhibited the desired ability to carry some stress after crack initiation. Infiltration of preforms containing 25 vol % chopped fibers at 1200°C for 12 h produced a composite with an overall density of 65% T.D. Testing of samples from this composite also resulted in flexure strengths less than 70 MPa (10,000 psi).

A typical as-infiltrated composite specimen consisting of SiC fibers infiltrated with Si_3N_4 is shown in Fig. 3. A scanning electron micrograph of the same type specimen is shown in Fig. 4. The interlocking of the fibers by the CVD Si_3N_4 is quite evident.

SiC FIBERS, SiC MATRIX

A parametric study examined the effect of several process variables on the deposition of the SiC matrix. The deposition temperature was varied from 1100 to 1500°C, the flow rate of the methyltrichlorosilane (MTS) feed material was varied from 25 to 200 cm^3/min, and the hydrogen flow was varied from 1 to 5 L/min. These conditions caused the hydrogen-to-MTS ratio to range from 10 to 50 and the run time to vary from 2 to 8 h. This range of conditions produced deposition rates from 0.2 to 0.9 g/h. The SiC deposited ranged in color from gray to yellow with some deposits containing metallic silicon. Nominal conditions now being used for deposition of SiC are 1200°C, an MTS (CH_3Cl_3Si) gas flow rate of 50 cm^3/min, a hydrogen-to-MTS ratio of 10, and a pressure of 100 MPa (1 atm). The SiC matrix was predominantly β-SiC, but the presence of α-SiC cannot be

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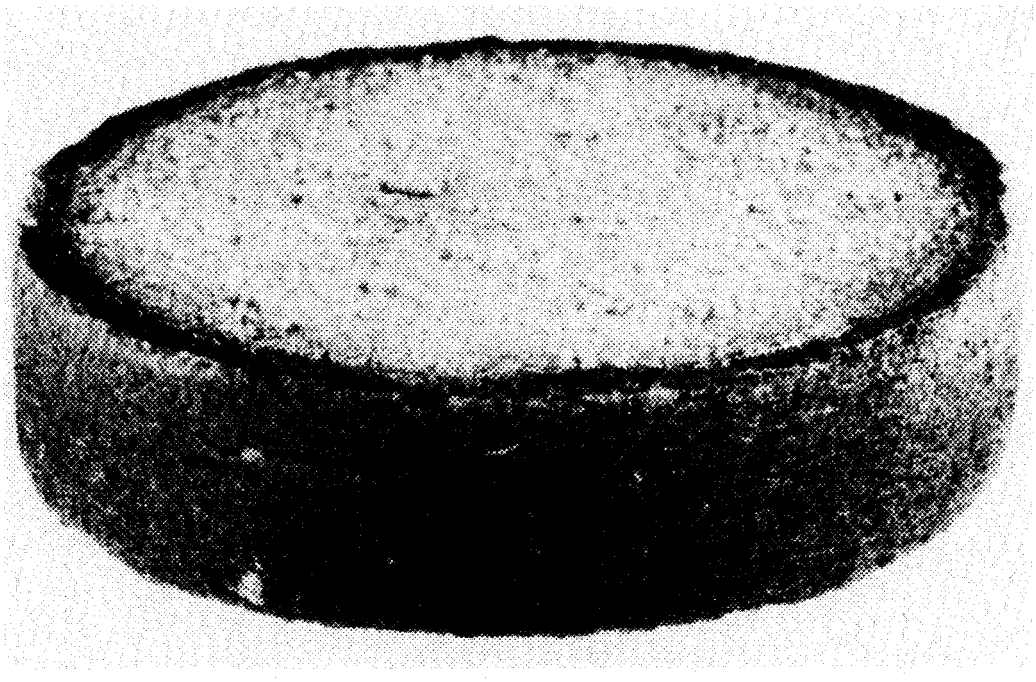

1 cm

Fig. 3. As-infiltrated composite specimen of SiC fibers in Si_3N_4 CVD matrix.

totally discounted because its major X-ray diffraction peaks coincide with those of β-SiC. The absence of minor α-SiC peaks verifies that α-SiC is present in quantities less than 10 vol %.

Most of the runs infiltrated SiC fibrous preforms with an SiC matrix. The preforms were fabricated from chopped fibers, stacked layers of cloth, or stacked layers of unidirectional fibers. The preforms had fiber contents ranging from 10 to 58 vol % and were infiltrated at 1200°C for 17 to 35 h. Composites were produced with densities ranging from 65 to 80% T.D., flexural strengths up to 476 MPa (69 ksi), and strain values up to 1%.

SiC Chopped Fibers, SiC Matrix

Fabrication data for composites with chopped fibers are summarized in Table 1. The small specimens listed in the table (specimens 29, 31, and 33) were difficult to infiltrate and showed only a slight increase in density. Apparently the injector cooled the small specimens sufficiently

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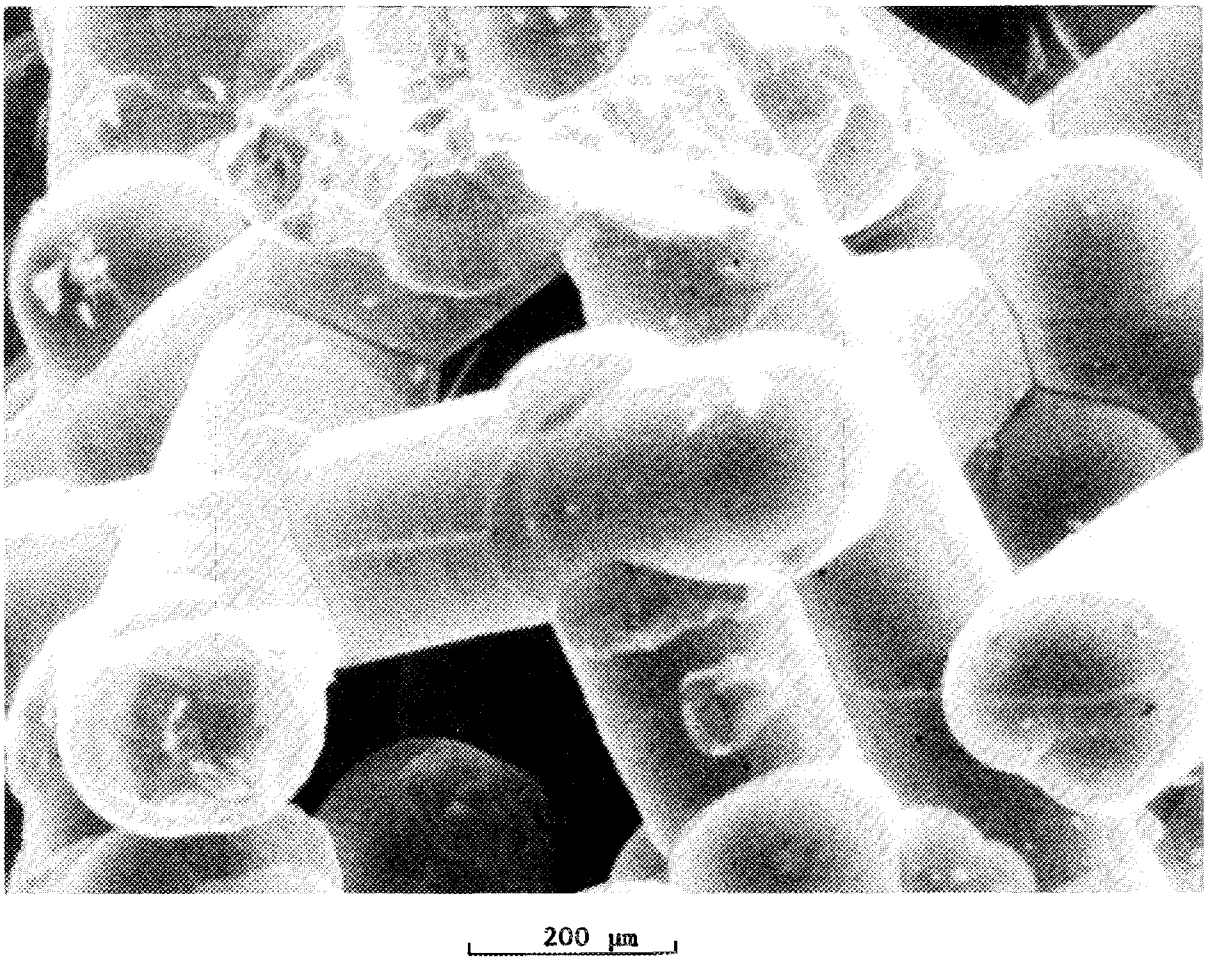

Fig. 4. Scanning electron micrograph shows interlocking of SiC fibers (10–15 μm diam) by deposition of a CVD Si_3N_4 matrix.

that deposition was very slow. The remainder of the information is for large vacuum molded specimens (45-mm diam) infiltrated at the nominal conditions, with any exceptions noted in the table. The preforms had fiber contents ranging from 17 to 25 vol % and were infiltrated at 1200°C for 6 h with axial flow and 12 h with axial plus radial flow. A composite (specimen 40) with a density of about 64% T.D. was obtained. Increasing the infiltration time to 21 h (specimen 44) increased the density to 70% T.D. Note that when the deposition temperature was reduced to 1100°C (specimen 45) a total of 41 h of infiltration was required to obtain a density of 72% T.D. A typical chopped-SiC-fiber composite is shown in Fig. 5 (specimen 38, Table 1) both as formed and as infiltrated.

Table 1. Data summary for composites of chopped SiC fibers in SiC CVD matrix

Specimen		Preform		CVD infiltration								Flexure tested
						Axial flow		Axial plus radial flow			Total run time (h)	
Number	Size[a]	Fiber content (vol %)	Density (g/cm^3)	Gas flow (% of nominal)[b]	Temperature (°C)	Time (h)	Density (g/cm^3)	Time (h)	Density (g/cm^3)	Density (% T.D.)		
29	Small	54.0[c]	1.38	200	1200	4	1.55	None	None	54.3	4	Yes
31	Small	23.1	0.59	50	1200	11	1.02	None	None	33.4	11	Yes
33	Small	20.1	0.51	100	1200	5	0.77	19	1.15	37.4	24	Yes
35	Large	16.8	0.43	100	1200	6	1.01	11	1.95	62.9	17	Yes
38	Large	24.3	0.62	100	1200	6	1.06	12	1.94	63.6	18	Yes
40[d]	Large	25.4	0.65	100	1200	6	1.20	12	1.95	64.1	18	Yes
44[e]	Large	21.9	0.56	100	1200	12	1.56	9	2.16	70.5	21	Yes
45	Large	21.3	0.54	100	1100	27	1.79	14	2.22	72.3	41	Yes
59	Large	25.0[f]	0.67	100	1200	4	0.91	21	2.01	65.1	25	No

[a]Small = 25 mm (1 in.) in diam by 4 mm (0.16 in.) thick; large = 45 mm (1.75 in.) in diam by 12 mm (0.5 in.) thick.

[b]Nominal flows are: methyltrichlorosilane, 50 cm^3/min; hydrogen, 500 cm^3/min.

[c]Wet preform was die pressed to produce high fiber content.

[d]Preform precoated with BN in CVD furnace before infiltration.

[e]Chopped fibers precoated with BN before fabrication of preform.

[f]Chopped NICALON fibers made up 75% of the fibers, and 25% were SILAR whiskers.

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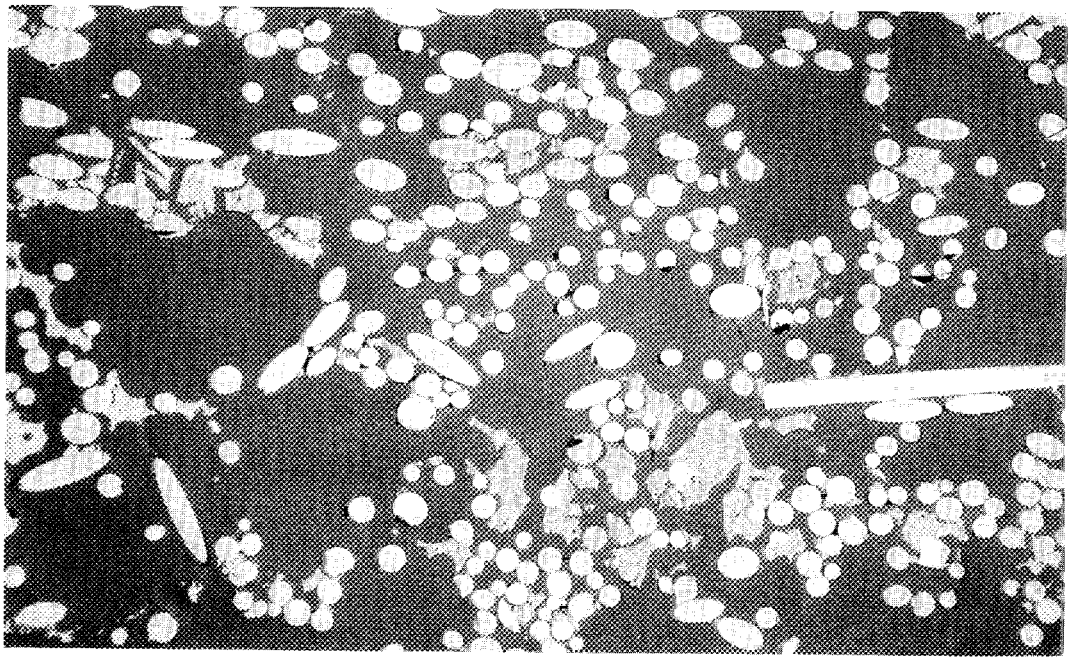

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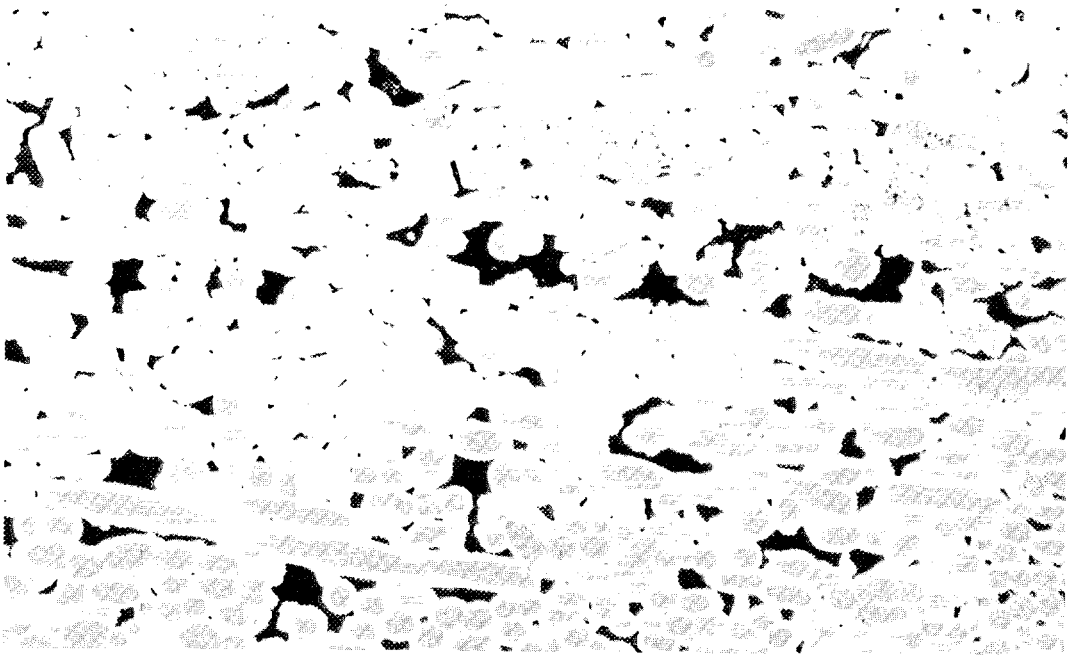


Fig. 5. Typical SiC composite fabricated from a chopped-fiber preform (specimen 38, Table 1). The density of the fibrous preform was 24%, and that of the infiltrated composite was 64%.

High-strength vacuum-molded preforms fabricated from SiC whiskers (SILAR)* were also infiltrated. The initial moldings had whisker contents of only 10 to 15 vol % but had extremely low permeabilities, which made infiltration very difficult. A preform was made from a combination of SILAR whiskers and chopped NICALON† fibers in an attempt to produce a gas-permeable preform. As noted in Table 1, the preform (specimen 59) contained a total of 25 vol % fibrous material, of which 75% was chopped NICALON and 25% was SILAR whiskers. The permeability was still rather low: 25 h of infiltration increased the density to only 65% T.D.

Flexural strength data for composites made with chopped SiC fibers are shown in Table 2. These composites have rather low strengths [53 to 177 MPa (7.6 to 25.6 ksi)]. The chopped-fiber preforms had a low fiber content (15–25 vol %) but were infiltrated to a density comparable to that of composites reinforced with cloth or unidirectional fibers (70–80% T.D.). The chopped-fiber specimens obviously suffer from the low fiber content and have considerably less fiber pull-out (Fig. 6) because of the short fiber lengths.

SiC Cloth, SiC Matrix

Fabrication data for composites with SiC cloth are summarized in Table 3, and a typical specimen is shown in Fig. 7. The higher fiber content (40 to 45 vol %) characteristic of the cloth composites (specimens 54 and 57) is evident. The density of specimen 57, which was infiltrated at 1200°C for 24 h with methyltrichlorosilane, could not be calculated because a large excess of SiC deposited on the hot face of the composite. However, as discussed below, the flexure samples obtained from this composite had densities ranging from 75 to 90% T.D. The density and flexural strength data for cloth-reinforced composites are shown in Table 4. Of all the specimens discussed here, the highest strength was obtained from one formed by using cloth. As shown in Table 4, a sample from the middle of this specimen had a strength of 476 MPa (69.0 ksi) at an infiltrated density

*Arco Chemical, Greer, South Carolina.

†Nippon Carbon Company, Tokyo, Japan.

Table 2. Mechanical properties of composites of chopped SiC fibers in SiC CVD matrix

Specimen		Preform fiber content (vol %)	Flexural sample[a]				
Number	Size[b]		Sample location	Density		Flexural strength	
				(g/cm^3)	(% T.D.)	(MPa)	(ksi)
29	Small	54.0[c]	Middle	1.97	69.0	99	14.3
31	Small	23.1	Middle	2.07	67.7	111	16.1
33	Small	20.1	Middle	2.43	78.9	150	21.8
35	Large	16.8	Top	2.57	82.9	106	15.4
			Middle	2.21	71.3	62	9.1
			Middle	2.33	75.2	58	8.5
			Bottom	2.15	69.4	76	11.0
			Bottom	2.19	70.7	61	8.8
38	Large	24.3	Top	2.32	76.1	74	10.8
			Top	2.38	68.0	98	14.3[d]
			Top	2.38	68.0	88	12.8
			Middle	2.13	69.8	83	12.0
			Middle	2.19	71.8	87	12.6
40[e]	Large	25.4	Top	2.47	81.0	177	25.6
			Top	2.57	84.1	119	17.2
			Middle	2.23	73.2	170	24.6
			Bottom	1.57	51.4	90	13.0
44[f]	Large	21.9	Top	2.38	77.7	94	13.6
			Top	2.48	80.8	86	12.5
			Middle	2.19	71.3	74	10.7
			Bottom	2.24	73.1	53	7.6
45[g]	Large	21.3	Top	2.50	81.5	103	14.9
			Top	2.58	84.0	106	15.4

[a]Measured at room temperature by four-point bend test.

[b]Small = 25 mm (1 in.) in diam by 4 mm (0.16 in.) thick; large = 45 mm (1.75 in.) in diam by 12 mm (0.5 in.) thick.

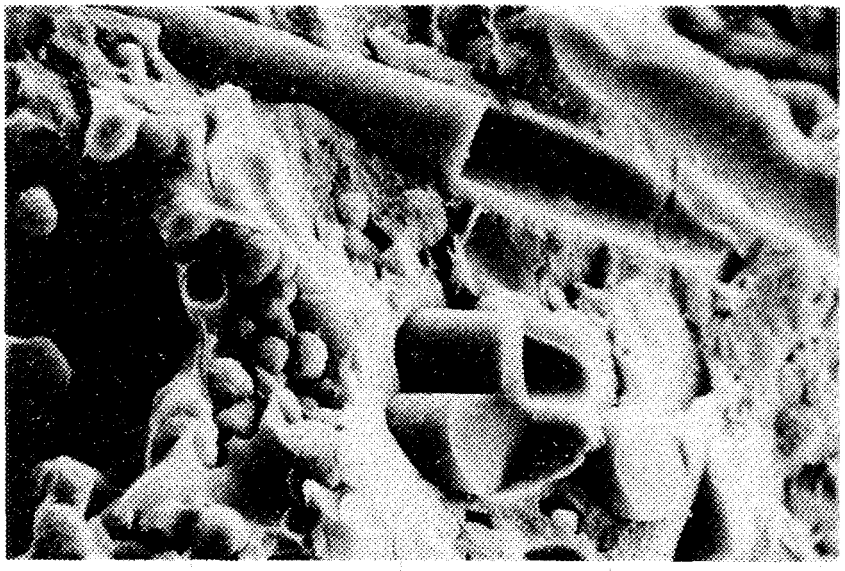
[c]Die pressed to produce high fiber content.

[d]Measured at room temperature by three-point bend test.

[e]Preform precoated with BN in CVD furnace before infiltration.

[f]Chopped fibers precoated with BN before fabrication of preform.

[g]Infiltrated at 1100°C.



10 μm

Fig. 6. Typical composite fabricated by infiltrating a chopped-fiber preform with SiC. Note the small amount of fiber pullout.

of 80.7% T.D. A sample from the top of the same specimen had a strength of 437 MPa (63.3 ksi) at a density of 90.3% T.D., and a sample from the bottom had a strength of 419 MPa (60.8 ksi) at a density of 75.3% T.D. Unfortunately, these samples with high strength values did not have particularly high strain values.

Methylsilane was used in run 54 to determine the effect of lower deposition temperatures on composite strength. The preform contained 45 vol % fibers and was infiltrated at 900°C for 14 h to a final density of 64% T.D. We suspected that the previously cited deposition conditions may damage the fibers and reduce their strength. Unfortunately the lower processing temperature for run 54 did not corroborate this hypothesis because the flexure strengths of the samples were quite low (Table 4). The highest strength [169 MPa (24.5 ksi)] observed in this composite group was obtained from the bottom sample. Samples from the top and middle had lower strengths of 107 MPa (15.5 ksi) at higher densities of 72 to 79% T.D.

Table 3. Data summary for composites of SiC cloth and SiC unidirectional fibers in SiC CVD matrix

Specimen[a]		Preform		CVD infiltration								Flexure tested
						Axial flow		Axial plus radial flow				
Number	Type fibers	Fiber content (vol %)	Density (g/cm^3)	Gas flow (% of nominal)[b]	Temperature (°C)	Time (h)	Density (g/cm^3)	Time (h)	Density (g/cm^3)	Density (% T.D.)	Total run time (h)	
54	Cloth[c]	45.1	1.15	*d*	900	7	1.75	7	1.87	64.2	14	Yes
57	Cloth[c]	41.6	1.06	100	1200	13	2.46	11	*e*	*e*	24	Yes
42	Uni-directional	57.7	1.47	20	1200	10	1.65	20	2.01	71.0	30	Yes
46	Uni-directional	45.1	1.15	50	1200	21	2.08	10	2.33	80.0	31	Yes
50	Uni-directional	45.5	1.16	100	1100	24	2.09	15	2.32	79.7	39	Yes
60	Uni-directional	39.5[f]	1.01	100	1200	21	2.31	12	2.77	94.3	33	Yes

[a]All specimens 45 mm (1.75 in.) in diam by 12 mm (0.5 in.) thick.

[b]Nominal flows: methyltrichlorosilane, 50 cm^3/min; hydrogen, 500 cm^3/min.

[c]Plain-weave cloth, 0-90° fiber orientation between layers.

[d]Methylsilane used for this experiment.

[e]Density calculation not available.

[f]NICALON continuous fibers precoated with thin layers of BN (Synaterials Co., Herndon, Va.) before fabrication of preform.

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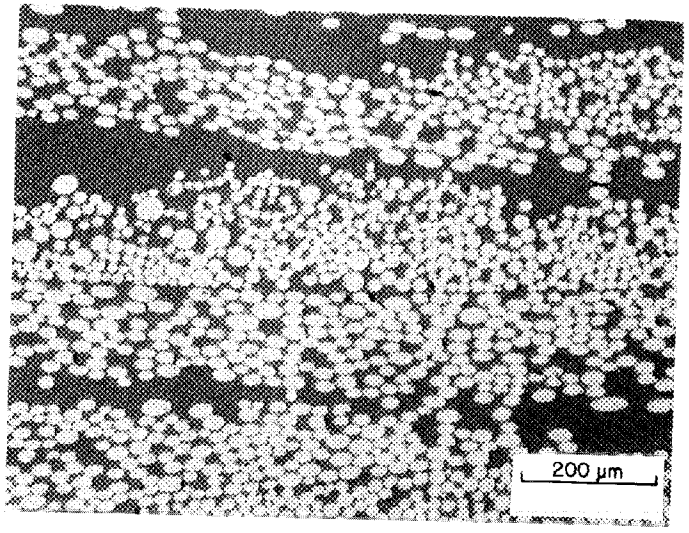

(*a*)

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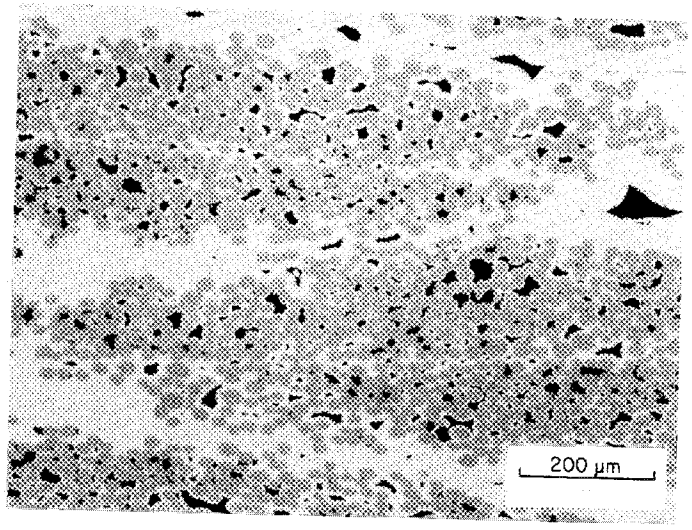

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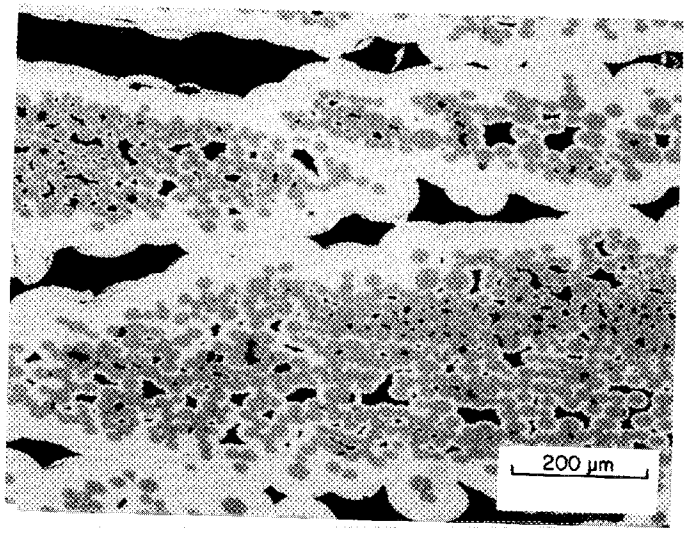

(*c*)

Fig. 7. (*a*) SiC cloth-fiber preform. (*b*) As infiltrated with SiC. (*c*) Porosity at layer cross-over.

Table 4. Mechanical properties of composites of SiC cloth and SiC unidirectional fibers in SiC CVD matrix

Specimen		Preform fiber content (vol %)	Flexural sample[a]				
			Sample location	Density		Flexural strength	
Number	Type fiber			(g/cm^3)	(% T.D.)	(MPa)	(ksi)
54[b]	Cloth[c]	45.1	Top	2.31	79.4	107	15.5
			Middle	2.09	71.6	107	15.5
			Bottom	1.87	64.3	169	24.5
57	Cloth[c]	41.6	Top	2.65	90.3	437	63.3
			Middle	2.37	80.7	476	69.0
			Bottom	2.21	75.3	419	60.8
42	Unidirec-tional	57.7	Top	2.17	76.7	159	23.0
			Top	2.19	77.4	268	38.9[d]
			Middle	2.18	77.0	110	15.9
			Bottom	2.07	73.2	330	47.8
46	Unidirec-tional	45.1	Top	2.02	69.4	118	17.1
			Top	2.09	71.8	100	14.5
			Middle			61	8.8
			Bottom	2.20	75.8	38	5.6
50[e]	Unidirec-tional	45.5	Top	2.05	70.4	230	33.4
			Middle	2.02	69.4	223	32.3
			Bottom	2.26	77.7	213	30.8
60[f]	Unidirec-tional	39.5	Top	2.01	68.3	257	37.2
			Middle	2.02	68.6	224	32.5
			Bottom	2.22	75.4	410	59.4

[a]Measured at room temperature by four-point bend test.

[b]Infiltrated at 900°C by using methylsilane.

[c]Plain-weave cloth, 0-90° fiber orientation between layers.

[d]Measured at room temperature by three-point bend test.

[e]Infiltrated at 1100°C by using methyltrichlorosilane.

[f]NICALON fibers precoated with thin layer of BN (Synaterials Co., Herndon, Va.) before fabrication of preform.

SiC Unidirectional Fibers, SiC Matrix

Fabrication data for composites with with unidirectional SiC fiber reinforcement are summarized in Table 3. The unidirectional preforms have the potential for the highest fiber content because of more efficient packing of fibers. However, at the highest fiber content (58 vol %) the preforms had very low permeability. This necessitated reduction of the fiber content to 40 or 45 vol %, which increased the permeability sufficiently to allow infiltration. Infiltration at 1200°C for about 30 h resulted in composite densities in the range of 70 to 80% T.D. When the deposition temperature was reduced to 1100°C, an infiltration time of 39 h was required to obtain a density of 80% T.D. A typical SiC unidirectional-fiber preform and composite are shown in Fig. 8.

The flexural strength data for the unidirectional-fiber composites are shown in Table 4. A sample from the bottom of specimen 42 (57.7 vol % fibers) had an infiltrated density of 73.2% T.D. and a fracture stress of 330 MPa (47.8 ksi) with a strain of 1.05%. In addition, the sample maintained 82.3% of this stress [272 MPa (39,400 psi)] at 1.65% strain and maintained 56.8% of this stress [188 MPa (27,200 psi)] at 2.84% strain. This exceptional stress-strain behavior and a comparison with that of normal monolithic SiC are shown in Fig. 9. Strain values were calculated from displacement of the testing machine cross head. These results have demonstrated that ceramic-ceramic composites can have a significant ability to carry a load after crack initiation. The extensive fiber pullout at the tensile fracture surface of this sample is shown in Fig. 10. Figure 11 shows the flexure sample unsevered after extensive deflection. Note from Table 4 that the other samples from this composite specimen had strengths ranging from 110 to 268 MPa (15.9 to 38.9 ksi) at densities of about 77% of T.D. Also shown in Table 4 is another unidirectional-fiber specimen (50) that had a strength of about 223 MPa (32 ksi) at densities of 70 to 78% T.D. and very little strength variation in samples from the top, middle, and bottom. Note that the matrix was deposited at 1100°C. Another unidirectional-fiber specimen (46) had strengths varying from 38 to 118 MPa (5.6 to 17.7 ksi) at densities varying from 70 to 75% T.D.

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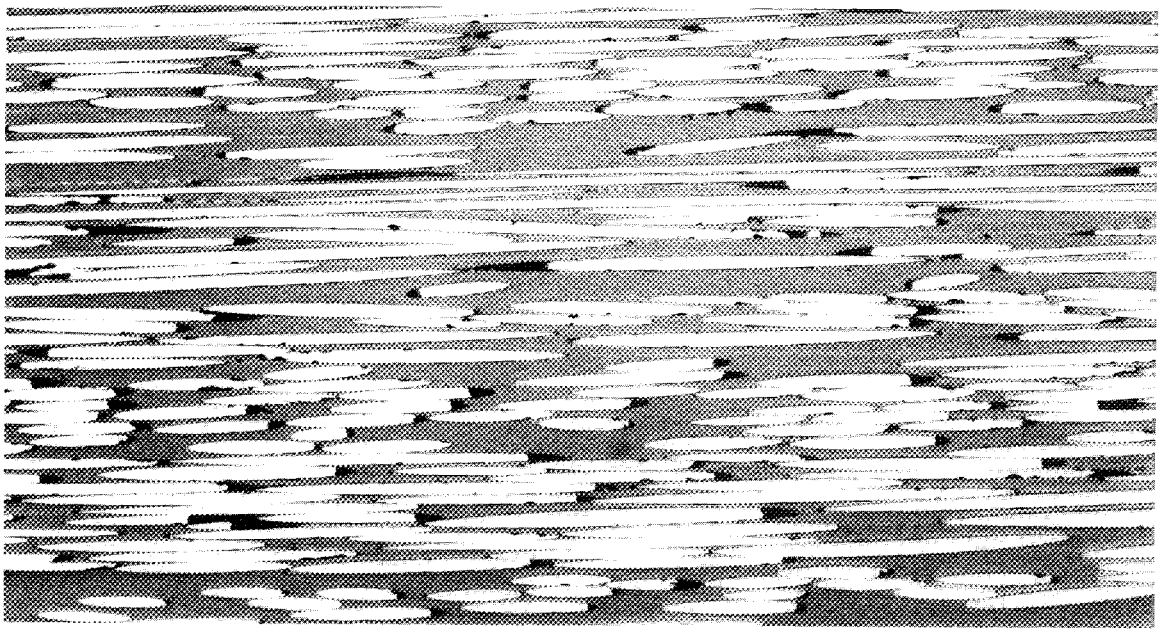

(*a*)

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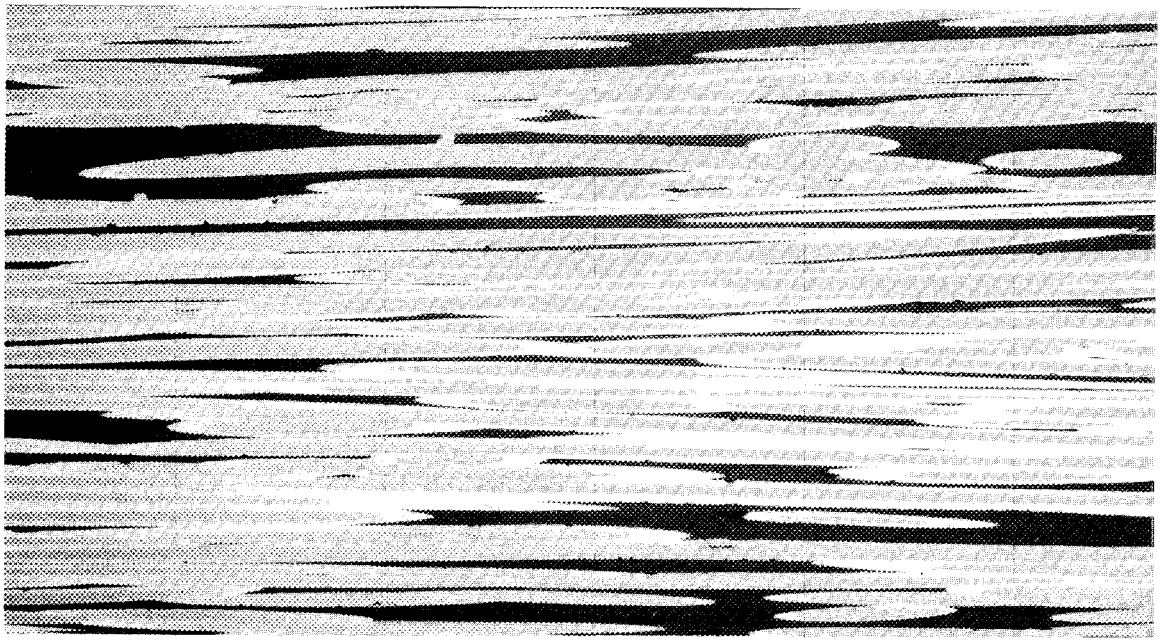

(*b*)

200 μm

Fig. 8. (*a*) SiC unidirectional-fiber preform. (*b*) As infiltrated with SiC.

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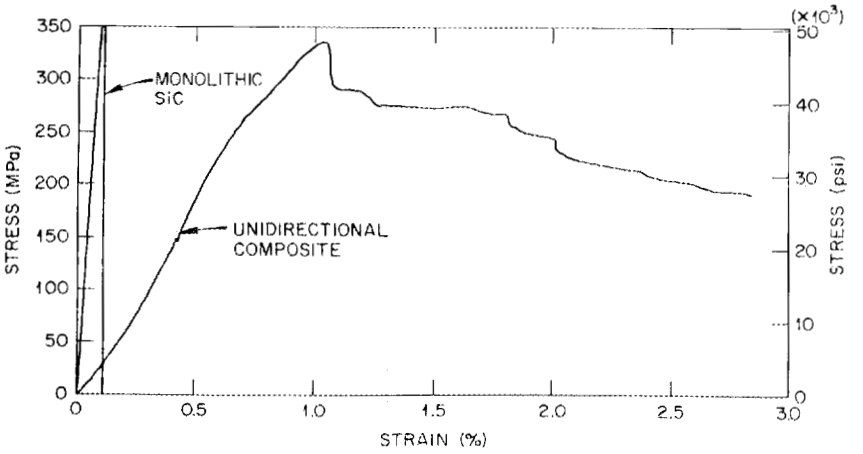
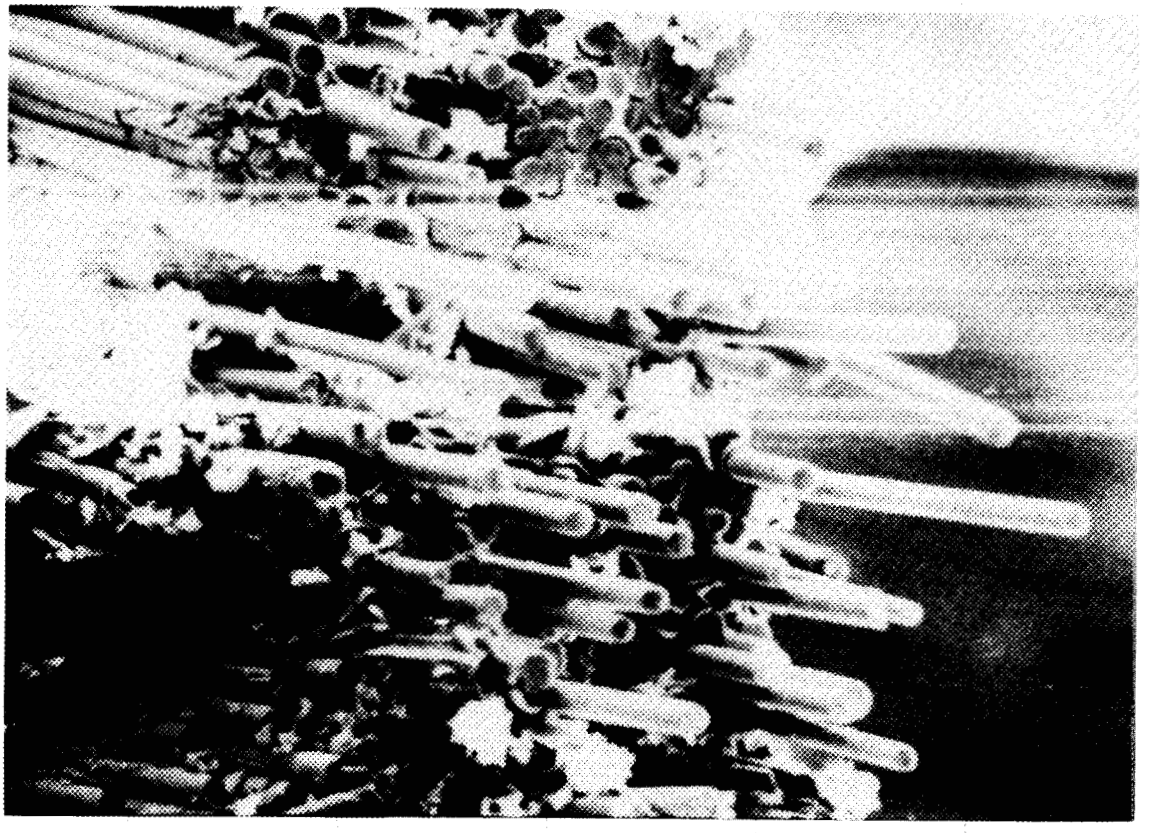


Fig. 9. Composite of unidirectional SiC fibers in an SiC CVD matrix was more strain tolerant than was monolithic SiC.

ORNL-PHOTO 8128-84



100 μm

Fig. 10. Fracture surface of a composite flexure sample with unidirectional SiC fibers in an SiC CVD matrix shows extensive fiber pullout.

ORNL-PHOTO 0247-85

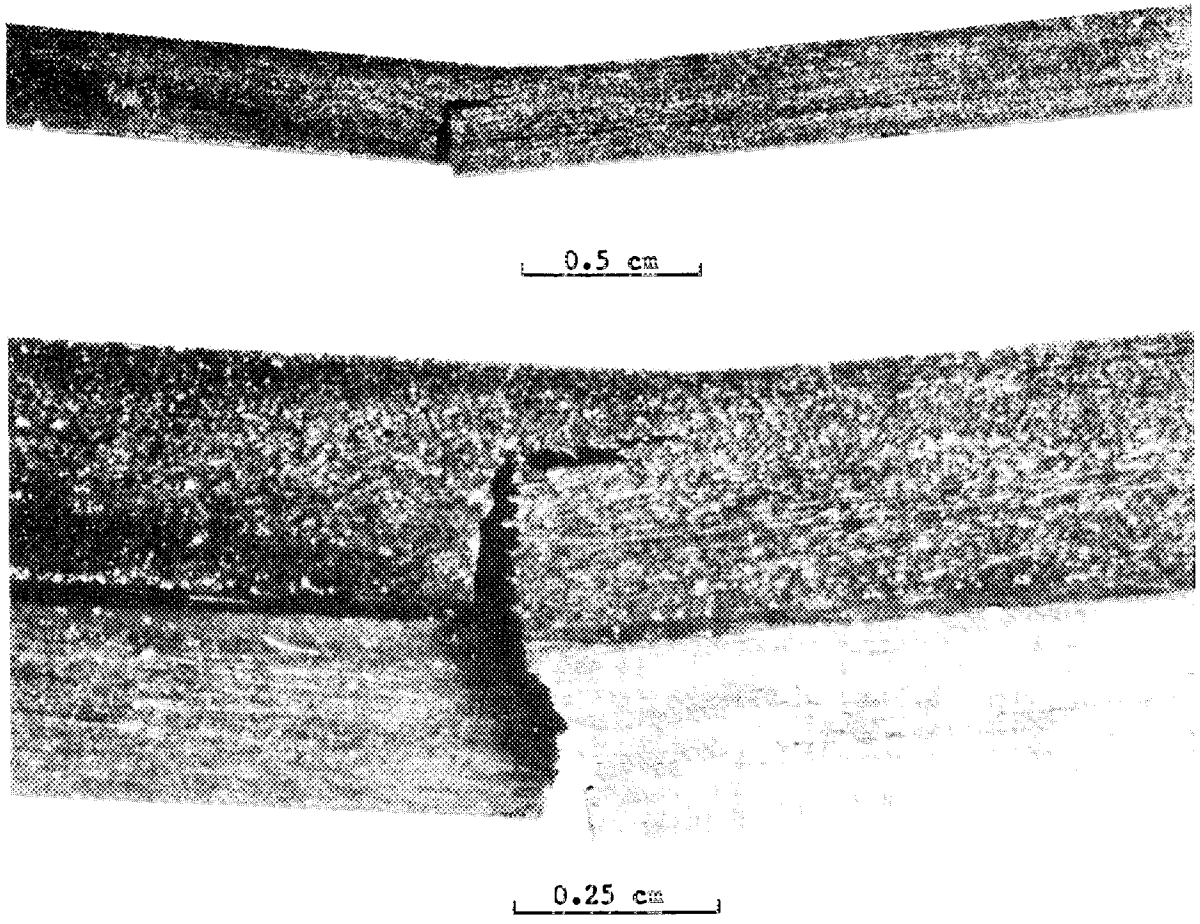


Fig. 11. Flexure sample of unidirectional SiC fibers in SiC CVD matrix was unsevered after extensive deflection.

FRACTURE TOUGHNESS

In addition to strength, the fracture toughness of the composites is a prime consideration. The concept of fracture toughness, and the various fracture toughness measurement techniques, may not apply to these materials because of their nonlinear elastic behavior. However, toughness measurements were made by using a single-edge notched beam in three-point bending. Initial tests were performed on monolithic SiC for comparison purposes. A flexural strength of 360 MPa (52,000 psi) and a toughness value of 3.8 $MPa \cdot m^{1/2}$ verified that the system was operating as expected. The unidirectional-fiber samples previously mentioned (from specimen 42) that exhibited high stress and strain values were expected to have higher toughness values than the monolithic SiC. However, the toughness values obtained were about 3.5 $MPa \cdot m^{1/2}$. The values for the vacuum-molded, chopped-fiber specimens also were in this range. Future work will include evaluations of other approaches for determining the fracture energy of these composites, such as the double cantilever beam technique.

Increased fracture toughness values for ceramic composites can be obtained when the fibers pull out of the ceramic matrix. Energy is absorbed as the fibers pull out of the matrix, causing the cracks to be deflected or blunted. Obviously, the bonding between the SiC fibers and the matrix is critical in determining the mechanical properties of the composites. If the bonds are too strong, cracks propagate through the matrix and fibers without interruption. Therefore, the composite exhibits brittle behavior (low fracture toughness), and the strength of the composite is controlled by the strength of the matrix or fiber — whichever is lower. Bonds that are too weak fail to transfer the load to the fibers, and the strength is controlled by the strength of the matrix. Therefore, we must learn to control the strength of the bonds between the matrix and the fiber. One potential method of modifying the bond strength is to coat the SiC fibers or whiskers with a thin layer of a material that will alter the bond between the matrix and coating or between the coating and fiber.

We coated SiC fibers with boron nitride and pyrolytic carbon to evaluate this concept.

Boron nitride coatings were applied to the SiC fibers at temperatures between 1100 and 1200°C by using BCl_3 and NH_3. Several composites were formed from BN-coated fibers. A chopped-fiber preform was coated with BN in the CVD furnace before infiltration (Table 1, specimen 40). Another preform (Table 1, specimen 44) was made from chopped fibers that had been coated with BN before fabricating the preform. Unfortunately, the strengths of these composites were no better than those of composites made from uncoated fibers.

A unidirectional-fiber specimen (Table 3, specimen 60) was formed from continuous NICALON fibers coated with a thin layer of BN (Fig. 12) by the Synterials Co. of Herndon, Virginia. These fibers were coated at temperatures less than 1000°C to minimize damage during processing. The flexure strength of this composite was comparable to that of the other unidirectional-fiber composites; however, the sample from the bottom of the composite had very high strength. The effect of coating the fibers with BN before infiltration is not yet clear and will be studied in more detail.

Pyrolytic carbon coatings deposited from C_3H_6 and H_2 have the advantage of reducing the possibility of fiber degradation because of the absence of chlorine from the process. Uniform coatings about 1.0 μm thick were applied to the fibers, but debonding occurred between the fibers and the coating because of a thermal expansion mismatch (Fig. 13). This debonding might allow the fibers to pull out of the matrix as desired. Composites containing these fibers are being processed and will be reported on later.

FIBER STRENGTH

The ability of the NICALON fibers to retain their strength during processing into ceramic-matrix composites is a prime consideration in optimizing their mechanical properties. Therefore, the effect of various process steps on fiber strength was investigated. Tensile testing of fiber tows[28] indicated that the strength of as-received fibers was about 1565 MPa (227 ksi). Heating the fibers at 1200°C for 1 h in argon (the last process step before infiltration) reduced the strength by about 60%

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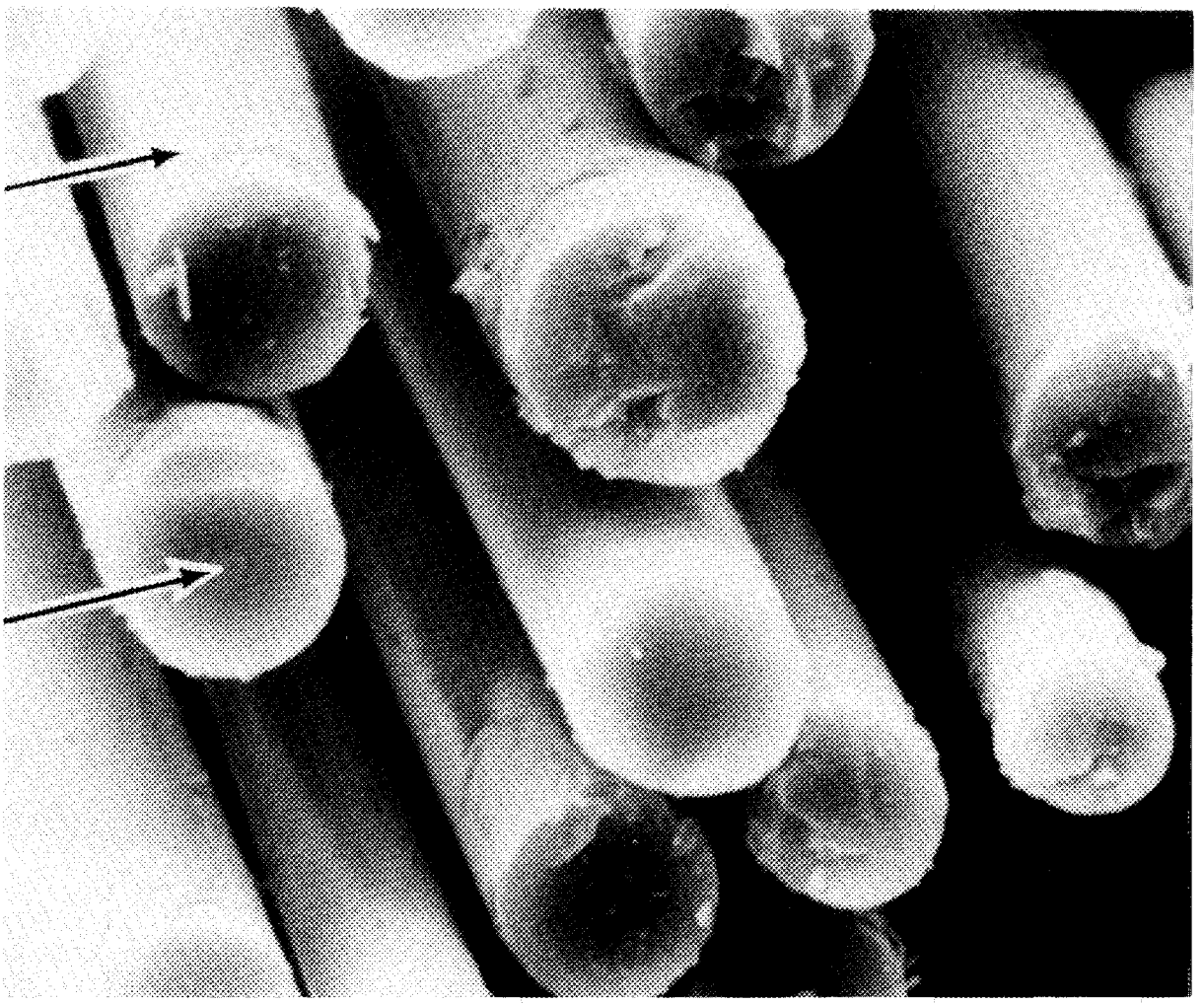

10 μm

Fig. 12. NICALON SiC fibers coated with a thin layer of boron nitride.

to 628 MPa (91 ksi). The strength of the fiber bundle (tow) is impossible to determine in an infiltrated composite. Therefore, we tested fiber tows in a separate furnace to simulate infiltration conditions. Fibers coated with a thin layer of CVD SiC by using the same conditions as in the CVD infiltration furnace were so brittle that they broke during handling and

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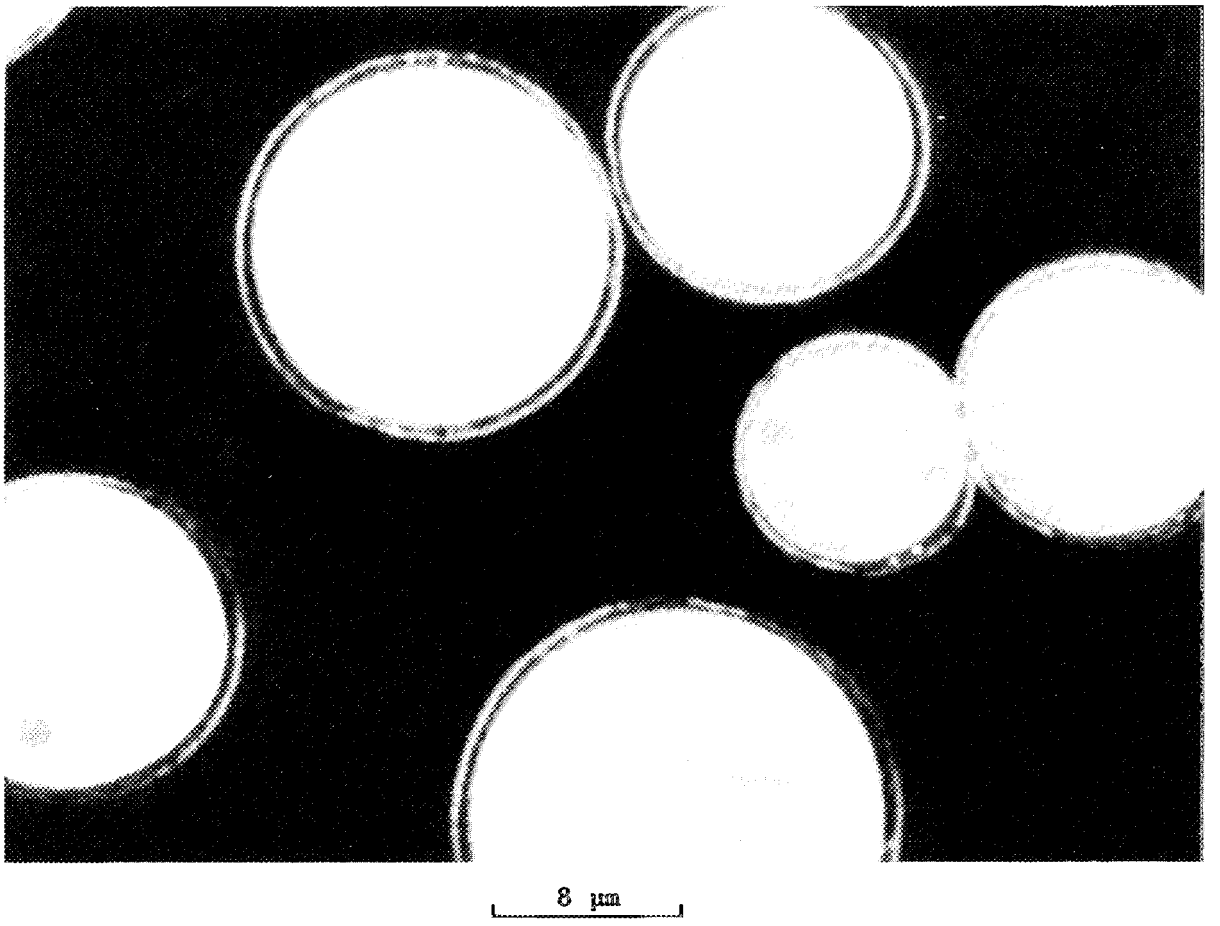

Fig. 13. NICALON fibers coated with a thin layer of pyrolytic carbon and sectioned end-on. Debonding occurred between the fibers and the coating.

could not be strength tested. Because large quantities of hydrogen are used in the infiltration process, the fiber tows were heated in hydrogen at 1200°C for 1 h. This also resulted in a 60% reduction in strength. Apparently the exposure to 1200°C for extended periods or the volatilization of impurities in the NICALON fibers influences the strength degradation. A new "ceramic grade" of NICALON fibers reported to have better high-temperature properties than those of the "standard grade" also was studied. Testing of as-received fibers of the ceramic grade gave essentially the same strength (within 5%) as the standard grade. Fibers treated

at 1200°C in argon or hydrogen for 1 h lost about 50% of their strength, as compared with a 60% loss for the standard grade. Preliminary testing of the ceramic fibers coated with SiC (including very careful handling) still indicated a drastic loss of strength (about 80%). Experimentation is continuing to determine the effect of many variables on fiber strength.

CONCLUSIONS

Ceramic-fiber–ceramic-matrix composites were prepared by fabricating an SiC fiber preform and then forming the ceramic matrix by infiltration with a chemical vapor deposition process. The infiltration time was reduced significantly (hours instead of weeks) by using a process that simultaneously utilized a thermal gradient and forced gas flow. Disks (50 mm in diam by 12 mm thick) of various types of SiC fiber preforms were prepared by vacuum molding of chopped fibers and by the stacking of layers of cloth or unidirectional fibers. The flexibility of the process was shown by the deposition of either an Si_3N_4 or SiC matrix and by the infiltration of both disk and tubular preforms to a density of 85% by using equipment designed especially for this concept.

Vacuum-molded preforms with densities of 15 to 25% T.D. were infiltrated in 24 h to produce composite densities of 60 to 70% T.D. Preforms fabricated of cloth or of unidirectional fibers had a higher fiber content (40 to 58 vol %) and required about 30 to 33 h of infiltration to produce composite densities of 70 to 80% T.D. Reducing the deposition temperature from 1200° to 1100°C increased the infiltration time to about 40 h.

Another major goal of this work was achieved by obtaining composites with improved mechanical properties. The strongest composite sample had a flexural strength of 475 MPa (69.0 ksi) and a strain of about 0.5%. This composite was formed by using an SiC cloth preform containing 42 vol % fibers and infiltrating the preform with SiC to a final composite density of 81% T.D. The highest strength of composites with unidirectional fiber reinforcing was only slightly less at 410 MPa (59,400 ksi). This composite contained 40 vol % fibers and was infiltrated to a density of 75% T.D. Another unidirectional-fiber composite (containing 58 vol % fibers) with a

strength of 330 MPa (47.8 ksi) had a strain of 1.05%, the highest of all the samples tested. This flexural testing demonstrated that ceramic-fiber—ceramic-matrix composites can carry a significant stress after the maximum stress has been reached and therefore can avoid brittle fracture. The specimen with 1% strain maintained 57% of its maximum strength at a strain of nearly 3% (calculated from ram displacement in four-point flexure), and it deformed significantly but did not break. The ability to maintain significant stress at high strain values was a major goal of this effort.

As overall development of the process continues, modifications that appear to improve the mechanical properties will be emphasized. They include fiber-matrix bonding and avoiding loss of fiber strength during processing. In addition, fracture energy measurement methods for these materials must be improved and validated.

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