A METHOD FOR RAPID CHEMICAL VAPOR INFILTRATION OF CERAMIC COMPOSITES
T. Besmann, R. Lowden, D. Stinton, T. Starr

To cite this version:

HAL Id: jpa-00229552
https://hal.archives-ouvertes.fr/jpa-00229552
Submitted on 1 Jan 1989

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L’archive ouverte pluridisciplinaire HAL, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d’enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.
A METHOD FOR RAPID CHEMICAL VAPOR INFILTRATION OF CERAMIC COMPOSITES

T.M. BESMANN, R.A. LOWDEN, D.P. STINTON and T.L. STARR*

Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6063, U.S.A.
*Georgia Tech Research Institute, Atlanta, GA 30332, U.S.A.

Abstract - Processes for the preparation of composite bodies using chemical vapor deposition have been developed at Oak Ridge National Laboratory (ORNL). Composites are prepared by infiltrating ceramic fiber preforms, held at elevated temperatures, with reactant gases that decompose to deposit ceramic matrix material between and around the fibers. The ORNL process is a marked improvement over those commonly in use; preforms that previously required weeks to densify now require ~24 h. Specimens with densities up to 90% of theoretical and strengths in the range of 400 to 450 MPa have been produced. Most importantly, the materials fail noncatastrophically, exhibiting typical composite behavior.

INTRODUCTION

A process for the rapid fabrication of continuous fiber-reinforced ceramic composites using chemical vapor deposition (CVD) to deposit the matrix material has been under development for several years (1-6). The process simultaneously utilizes thermal and pressure gradients to reduce infiltration time for centimeter-thick composites from weeks to <24 h and has subsequently been termed forced chemical vapor infiltration (FCVI). Disk shapes in excess of 4 cm in thickness and 1-cm wall-thickness tubes of continuous filament Nicalon\(^{(1)}\) uniformly infiltrated with SiC have been routinely fabricated by FCVI. These materials exhibit relatively high strain to failure with flexure strengths between 400 and 450 MPa.

It is the object of this paper to review recent efforts in the further development and optimization of the FCVI process with much of the detail left to the referenced papers. These efforts have included studies of the effect on infiltrated composites of fiber type and characteristics, and the use and nature of intermediate layers between the fiber and matrix. In addition, progress has been made in modeling FCVI such that infiltration times and uniformity are becoming predictable.

The baseline fiber used in process development for FCVI has been ceramic-grade Nicalon, a polymer-derived, amorphous SiC fiber. The strength of the fiber reinforcement in ceramic-ceramic composites has a significant affect on the overall mechanical properties. Nicalon is well known to lose strength when heated to above 1000 K (7,8). The implication is that the elevated processing temperature of FCVI can have a significant influence on the resultant strengths of infiltrated composites, and this was thus investigated.

As a result of the temperature sensitivity of Nicalon, and a desire to understand the properties of reinforcements with significantly different moduli, morphology, and chemical compositions (oxides), alternate reinforcing fibers have been explored. These fiber

\(^{(1)}\) Nippon Carbon, Tokyo, Japan
materials include FP, a crystalline alumina fiber; Nextel-440, a crystalline aluminoborosilicate fiber; and Tyranne, which is similar to Nicalon. FP fibers are of interest because of their high modulus (385 GPa) and potential for improvement in high-temperature creep. Unfortunately, the high modulus makes the fibers very fragile and difficult to handle or weave. Nextel fibers are of interest to the composite community because of their availability and ease of handling and weaving. Tyranne fibers were investigated because of their reported improved temperature stability over that of Nicalon. A second advantage of the Tyranne fibers is their smaller diameter (8 μm) compared to that of Nicalon (15 μm), which results in improved handling, weaving, and braiding behavior. Preliminary results of properties of FCVI composites containing these fibers are reported.

In evaluating the mechanical behavior of Nicalon/SiC composites fabricated early in the development of FCVI, both brittle failure and ductile composite fracture were observed in specimens produced under identical conditions. A thorough analysis of the fracture surface employing scanning and transmission electron microscopy and Auger electron spectroscopic (AES) analysis of heat-treated Nicalon fibers revealed a film composed of silicon and oxygen on the surface of the fibers. Examination of fracture surfaces of composites showed the fiber surfaces and fiber pull-out grooves to be oxygen rich. An intermediate coating applied to the fibers prior to infiltration has been seen to weaken the fiber-matrix bond and produce the crack deflection and fiber pull-out that contribute to the toughening of a composite.

Secondary ion mass spectroscopic analysis of composite samples fabricated from uncoated Nicalon fibers revealed higher concentrations of chlorine in the fibers than in the matrix. This suggests that the fibers may be chemically attacked by chlorides during matrix deposition (methyltrichlorosilane as the infiltration precursor), perhaps resulting in degradation of fiber properties. An intermediate coating may therefore be necessary not only to obtain satisfactory fiber pull-out but to protect the fiber during processing as well.

The affect of interfacial coatings has thus been investigated in the current work. Comparisons of strength and fracture behavior between infiltrated, uncoated Nicalon, and Nicalon precoated with silicon and various thicknesses of pyrolytic carbon have been made. Luthra (13) has suggested that silicon can stabilize the chemistry of Nicalon. Pyrolytic carbon has been used for some time to produce Nicalon fiber composites with improved strength and fracture behavior.

The efficient extension of the FCVI technique to large and complex shapes will require the use of a process model. Such an analytical model is being developed and centers on linking mass transport and reaction kinetics utilizing a finite volume approach. The model is briefly described in this report and the predicted infiltration times compared to experiment.

EXPERIMENTAL

The fabrication of SiC matrix composites by FCVI has been previously described in detail. Fibrous preforms are retained within a graphite holder that contacts a water-cooled gas distributor, thus cooling the reactant gas inlet side of the preform. The sides and opposite end of the preform are exposed to the hot zone of the furnace creating a steep temperature gradient across it. The reactant gases are forced under pressure into the cooled side of the fibrous preform but initially do not react because of the low temperature. The gases continue from the cooled portion of the preform into the hot portion, where the matrix begins to deposit on the fibers. Deposition of matrix material within the hot region of the preform increases the density; and, therefore, the thermal conductivity of the preform moves the deposition zone progressively from the hotter regions toward the cooler regions.

An FCVI developmental system has recently been provided with a computer interface and computer system for process control and data acquisition. Real-time control of process variables, such as temperature (furnace and coolant), reactant flows, and system pressure during infiltration, can allow continuous or discrete adjustment of the FCVI parameters to optimize the process.

---

(2) E.I. Du Pont de Nemours and Co., Wilmington, Delaware
(3) 3M Co., Minneapolis, Minnesota
(4) UBE Industries, Tokyo, Japan
(5) Camile 3000, Dow Chemical Co., Midland, Michigan
Preforms are fabricated by stacking multiple layers of cloth in graphite holders with each subsequent layer of cloth rotated 30° with respect to the previous layer. Preforms prepared in this manner had fiber contents ranging from 20 to 45 vol %, depending on the fiber type.

Thin coatings (~0.2 µm) were deposited on the fibers in the FCVI apparatus (without active cooling of the reactant gas entrance surface) to produce intermediate layers using SiH₄, diluted in argon as the source of silicon and propylene in argon as the source of carbon. The deposition conditions were 1675 K for silicon and 1375 K for pyrolytic carbon at 3 kPa total pressure. The presence of the coatings was confirmed by X-ray linescans of cross sections using a JEOL 733 electron microprobe or by polarized light optical micrography. For the infiltration of SiC, the reactant was methyltrichlorosilane (MTS) flowed at 0.33 g/min in hydrogen at 500 cm³/min using a nominal top (hot) surface temperature of 1473 K.

The standard mechanical property test used for comparison of fiber-reinforced composites is four-point flexure. Flexure bars were cut from the samples parallel to the 0 to 90° orientation of the top layer of cloth using a diamond saw, and tensile and compression surfaces were ground parallel to the long axis of the specimen. Layers of six specimens were normally obtained from the top, middle, and bottom for a total of 18 specimens per disk-shaped sample. The nominal dimensions of the bars were 2.5 × 3.3 × 45 mm and all were measured and weighed to determine densities. Flexural strengths were measured at room temperature using a support span of 25.4 mm, a loading span of 6.4 mm, and a crosshead speed of 0.051 cm/min. Specimens were loaded perpendicular to the layers of cloth.

The strength of the fiber-matrix bond was measured using a microindentation technique which has been thoroughly evaluated (10,11,17,18). This technique uses a microhardness indenter to apply a force to the end of a fiber embedded in a matrix. Interfacial shear stresses are determined from the applied load and displacement of the fiber and are computed from impression dimensions on the fiber end and the indenter contact points along the edge of the fiber cavity.

PROCESS MODELING

Modeling of FCVI processes is based on conservation equations for mass, energy, and momentum and has previously been described in some detail (15,16). These differential equations express in mathematical form the physical requirement that the total mass, energy, and momentum of a system is unchanged. Within a particular volume element, any change with time is equal to the difference between the flux in and the flux out. With densification times of several hours or more, the spatial variations in FCVI are much larger than the temporal variations. Thus, the steady-state approximation is appropriate, leading to a substantial simplification in solving the conservation equations.

Numerical techniques for solving the conservation equations will give a result for almost any value of their coefficients. Successful modeling depends on selection of values for these parameters that correspond to physical reality. Most of the experimental work with the FCVI process has utilized a disk-shaped preform with constant forced flow from the cool face to the hot face. This geometry is approximated by using one-dimensional forms for the conservation equations. Modeling of the process requires solution of both the mass and energy balance equations. Since the gas flow rate is currently held constant throughout infiltration, solution of the momentum equation is unnecessary except to define the end point of the process, which is a rise in the back pressure to a limiting value.

The temperature profile between the two constant temperature points (top and bottom surfaces) through the preform is determined by the thermal resistances of all intervening materials and interfaces. A steady-state thermal model for the FCVI system which divides the preform into a finite number of volume elements could thus be used. Additional thermal resistance elements connect the top and bottom of the preform to the constant temperature points. The effect of the gas flow is included separately. The temperature at each point can be calculated if the thermal resistance (or conductance) of each element is known.

For elements within the preform, thermal conductivity depends on the density, which varies from point to point and changes as infiltration proceeds. Experimental measurements of thermal diffusivity for composites with a range of densities are required. These are "series resistance" fit and the derived function is used in the model to compute the conductivity of each element within the preform. The thermal resistances of the elements above and below the preform are treated as adjustable parameters in the model and are set to match experimentally measured temperatures within the preform prior to the start of infiltration.
Examination of partially infiltrated composites has shown that FCVI proceeds as an extended fiber coating process. Most studies of the kinetics of coating by CVD, however, utilize temperatures higher than those for FCVI or involve bulk substrates where the mass transport processes are significantly different than for porous preform infiltration. For SiC deposited from MTS, fiber coating experiments yield a rate law which appears to be applicable to CVI (19). In excess H₂ and over the range 1100 to 1300 K, the linear deposition rate is first-order in MTS concentration and exponential in temperature. This rate is used directly in the FCVI model.

For the FCVI model a volumetric deposition rate is required. This is simply the linear rate from above multiplied by the surface area available for deposition within the finite volume. The initial preform surface area per unit volume depends only on the density and fiber diameter. As fibers are coated in the FCVI process, the surface area initially increases. Eventually, as porosity decreases, the surface area also decreases approaching zero at full density. For oriented fiber preforms, the microstructure is equivalent to two-dimensional growing, adjacent circles. The analysis does not take into account large-scale structure, such as the porosity between cloth layers. Such structure has little effect on the surface area function except at high densities where it contributes significant pore volume but minimal surface area.

RESULTS

Influence of Fibers--To investigate the affect of processing temperature on the strength of Nicalon/SiC composites prepared by FCVI, four sets of disk-shaped samples were fabricated at top (hot) surface temperatures of 1448 K, 1498 K (two samples), and 1548 K. A plot of the average flexure strengths of specimens cut from the uppermost portion (the volume which experienced the highest processing temperatures for the longest period) clearly illustrates the strength loss (Fig. 2). 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 FP, Nextel-440, and Tyranno fibers precoated with 0.2 μm of pyrolytic carbon (Table 1). Although composites fabricated with Nextel fibers were not as dense as those fabricated with FP fibers, the mechanical properties were better. (The FCVI process has not been optimized on these fiber systems, and this has caused the wide variation in density within the samples described in Table 1.) The load displacement curves for both Nextel-440 and FP cloth are shown in Fig. 3. Both composites exhibit toughening by fiber pull-out but the fracture is more brittle than for composites reinforced with Nicalon fibers.

The mechanical properties of composites reinforced with Tyranno fibers were very encouraging. Despite the somewhat less than optimum density of the fabricated composites, strengths greater than 350 MPa were obtained for samples from the top, middle, and bottom of the composite (Table 1). A load displacement curve for a Tyranno reinforced composite exhibits toughening by fiber pull-out; however, the fracture is again more brittle than for Nicalon composites (Fig. 3).

Fiber-Matrix Interface--Interfacial frictional stresses were measured using a micro-indentation technique. Hardnesses of the fibers, which are necessary for calculating the frictional stress, were 22.0 ± 0.7 GPa for Nicalon fibers and 15.0 ± 0.7 GPa for Nextel fibers. Interfacial shear stresses ranged from 0.6 MPa to 88 MPa. Average values of the interfacial shear stresses are given in Table 2 together with room temperature four-point flexure strengths. The composites prepared from uncoated Nicalon fibers and from Nicalon fibers coated with a thin film of elemental silicon exhibited low flexure strength. Typical load-deflection curves and scanning electron microscope photographs of the fracture surfaces of these composites are shown in Fig. 4. The specimens displayed brittle failure with no indication of toughening. The lack of fiber pull-out and the flat, smooth fracture surfaces of test specimens suggest complete failure of the reinforcement and/or a high degree of bonding between fiber and matrix. Indentation measurements confirmed the high interfacial frictional stresses and in some cases the loads were enough to cause splitting of the fiber and extensive cracking of the surrounding matrix.

The influence of the thickness of a pyrocarbon layer on the mechanical behavior of the Nicalon fiber-reinforced composite samples was also investigated (Table 2). The concentration of reactant propylene was varied to produce films that ranged in thickness from 0.07 to 0.5 μm. The specimens displayed gradual failure, as shown in the selected load-displacement curves in Fig. 5, and the thicker layers produced larger strain to failure with a maximum in strength at 0.17 μm pyrolytic carbon coating thickness (Table 2). The interfacial frictional stress was correspondingly found to decrease with increasing coating thickness.
The composite sample prepared from as-received Nextel-440 fibers exhibited brittle fracture and low strength. The fracture surfaces were smooth with no evidence of fiber pull-out. A carbon coating applied to the fibers resulted in improved strength and toughness. Extensive fiber pull-out led to increased strength and improved strain to failure (Table 2).

Process Modeling--Incorporating the individual model elements described above into an overall descriptive model for FCVI allows iterative calculation of composite density at each element as infiltration proceeds. Figure 6 shows a typical calculated infiltration run. Initial densification is most rapid at the hot face. As density increases, the temperature near the cool face rises, increasing the deposition rate. The decrease in available surface area and reagent depletion both tend to reduce the deposition rate near the hot face so that the density becomes more uniform during the latter stages of densification. The objective in obtaining uniformly dense composites is to have all volumetric elements simultaneously approach the same high value for density.

Also shown in Fig. 6 is a metallographic cross-section of a Nicalon cloth preform infiltrated for 6 h under the indicated conditions. As can be seen in the density-time plot at 6 h, the cold surface will have a considerably lower density than would the hot surface. This is confirmed experimentally in the metallograph which shows the hot (top) side to be significantly more dense than the cold (bottom) side. Comparisons made under other conditions and for different infiltration times show similar qualitative agreement.

Specification of the end point for infiltration is somewhat problematic in the model. Experimentally, the infiltration is considered complete when the back pressure in the gas injection system reaches a particular value (nominally -70 kPa). Additional modeling of this larger scale fiber structure is needed in order to accurately predict permeability during the final stages of densification. The end point for the model is currently chosen as that time when any one of the volume elements reaches 97% of full density.

DISCUSSION

The mechanisms of Nicalon fiber degradation have been the subject of extensive study (7,8,20-22). Heating fibers above 1000 K 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 evolution, carbothermal reduction of SiO\textsubscript{2} present in the fiber to SiC with mechanical damage due to CO evolution, and other compositional changes. It is clear from the observation of decreasing flexural strength with increasing processing temperature that such an affect is confirmed in the composites. This is particularly true in view of the measurements of increasing strength of chemical vapor deposited SiC with increasing deposition temperature (23-26).

The Nicalon fiber-reinforced composite samples fabricated from uncoated fibers and fibers precoated with silicon exhibited low strength and brittle fracture. The behavior appears to be due to a combination of strong fiber-matrix bonding and fiber property degradation. Similar mechanisms may be operating at the surface of untreated fibers in the Nicalon/SiC system which, as received, contain an intermittent silica layer (27).

The values for interfacial frictional stress for the samples containing uncoated Nicalon and Nextel fibers were relatively high, 47 ± 14 MPa and 76 ± 38 MPa, respectively. In comparison, reported shear stresses for Nicalon/glass composites with high strain to failure are 2.0 MPa (17). The high values are consistent with the mechanical behavior of Nicalon/SiC and Nextel/SiC composites with no interface coating which exhibit brittle, catastrophic failure.

A carbon layer deposited on fibrous preforms prior to densification improved the mechanical properties of Nicalon/SiC composites fabricated using FCVI techniques. Precoating fibers prior to matrix deposition not only reduces interfacial stresses, but may also provide protection from chemical attack during processing. Varying the thickness of the carbon layer decreases interfacial bonding and friction, and, therefore, improves matrix cracking stress and postfracture behavior.

The composite containing uncoated Nextel-440 fibers possessed low strength and no evidence of fiber pull-out. As in the Nicalon/SiC system, this behavior appears to be due to a combination of strong bonding and fiber property degradation. Nextel is an alumino-borosilicate fiber and may also be prone to chemical attack by the chloride byproducts that are generated during infiltration. The sample fabricated from carbon-coated Nextel fibers showed improved properties and reduced interfacial bonding. Again, the carbon probably
weakened the bonding and friction at the fiber-matrix boundary as well as protected the fibers from damage during processing.

The finite-volume model of FCVI was run with a variety of infiltration conditions for which experimental data are available (27). The calculations are in excellent agreement with experimental trends. Densification time decreases with increased temperature, increased MTS flow, and decreased H₂ flow. The density near the cool face increases with increased temperature and decreased H₂ flow. Comparison of calculated densification times with experimental times also indicate good agreement (Fig. 7). The significant deviations are likely due to poor characterization of actual FCVI conditions.

SUMMARY

Composites reinforced with continuous ceramic fibers are effectively fabricated by FCVI, and continued development has further optimized the process on Nicalon/SiC. Relatively high fracture toughnesses and moderate strengths are easily achieved. The evidence of the dependence of the strength of Nicalon/SiC composites on processing temperature will provide an impetus to use lower hot surface temperatures.

Composites produced from FP cloth exhibited relatively low strength, and the fragile and brittle nature of the fibers must be improved before composites can be commercially interesting. Composites fabricated from Nextel fibers showed promising results, exhibiting toughening by fiber pull-out. The strength of the material was somewhat low but could be improved by optimization of processing conditions and the interfacial bonding. The most promising results were obtained with Tyranno fibers. The strength of the material is at least as high as Nicalon-containing composites of similar density, and they exhibit similar strain tolerance. The potential for improvement in high-temperature behavior is currently being investigated.

The fiber-matrix interface in fiber-reinforced ceramic composites appears to play a large role in controlling strength and toughness. The indentation method has proven to be a simple method for the semi-quantitative comparison of the interfacial forces in fiber-reinforced composite materials except in cases of high shear strength. The calculated values have been related to observed and predicted fracture behavior. The limitations of the indentation method became apparent during testing of the silicon-coated fiber sample. The high shear strengths necessitated the application of large compressive loads on the fiber ends resulting in splitting or crushing of the fiber by the indenter.

Control of the interfacial bond in ceramic matrix-ceramic fiber composites can be used to optimize its properties. Whereas values for interfacial frictional stress for uncoated Nicalon and Nextel fibers are high and the composites exhibit little strain to failure, Nicalon/SiC and Nextel/SiC composites with sufficient carbon layers had low interfacial stresses and high strengths and pull-out, comparable to those observed in glass matrix composites. Appropriate carbon layer thicknesses can thus yield composites with high strengths (>400 MPa) and gradual failure behavior. Coatings can also be employed to protect the fibers from environmental degradation.

Modeling of the FCVI process has successfully predicted trends in infiltration rates that agree reasonably well with experimental values. The improved understanding of the parameters controlling densification that result from the model will allow extension of the process to more complex shapes and alternate reinforcements. Efforts have been initiated to develop a general three-dimensional model for more effectively modeling FCVI, as well as other CVI techniques. A computer has been interfaced with an existing FCVI developmental system for data acquisition and to provide for the real-time control required for optimizing the process.

ACKNOWLEDGMENTS

The authors appreciate the useful comments of J. I. Federer. P. H. Wilson is acknowledged for editorial services and C. A. Valentine and B. Q. Atkinson for manuscript preparation. H. R. Livesey provided the graphics. The research was sponsored by the U.S. Department of Energy, AR&TD Fossil Energy Materials Program, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

REFERENCES


### Table 1. Characterization of composites reinforced with continuous fibers.

<table>
<thead>
<tr>
<th>Fiber/sample number</th>
<th>Fiber content (vol %)</th>
<th>Sample location</th>
<th>Composite density (% theoretical)</th>
<th>Flexural strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FF/208</td>
<td>21</td>
<td>Top</td>
<td>85.9 ± 0.9</td>
<td>127.7 ± 21.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>74.7 ± 4.4</td>
<td>147.5 ± 28.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>78.9 ± 3.0</td>
<td>164.8 ± 19.2</td>
</tr>
<tr>
<td>Nextel-440/214</td>
<td>40</td>
<td>Top</td>
<td>75.7 ± 0.7</td>
<td>184.9 ± 56.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>73.7 ± 0.7</td>
<td>188.7 ± 8.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>66.7 ± 1.1</td>
<td>148.1 ± 21.4</td>
</tr>
<tr>
<td>Nextel-440/215</td>
<td>34</td>
<td>Top</td>
<td>75.6 ± 0.6</td>
<td>110.9 ± 10.8</td>
</tr>
<tr>
<td>Tyranno/242</td>
<td>43</td>
<td>Top</td>
<td>79.4 ± 1.8</td>
<td>395.4 ± 18.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>75.6 ± 0.2</td>
<td>395.0 ± 7.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>72.5 ± 0.5</td>
<td>351.9 ± 11.0</td>
</tr>
<tr>
<td>Tyranno/243</td>
<td>42</td>
<td>Top</td>
<td>81.0 ± 0.7</td>
<td>368.9 ± 7.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Middle</td>
<td>75.3 ± 0.1</td>
<td>364.2 ± 2.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bottom</td>
<td>64.4 ± 0.8</td>
<td>216.1 ± 36.5</td>
</tr>
</tbody>
</table>

### Table 2. Intermediate coatings and their effects on interfacial stress and mechanical behavior of composites.

<table>
<thead>
<tr>
<th>Fiber precoating</th>
<th>Thickness (μm)</th>
<th>Flexure strength (MPa)</th>
<th>Interfacial stress (MPa)</th>
<th>Observed behavior</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nicalon</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncoated</td>
<td>82 ± 10</td>
<td>48 ± 14</td>
<td>48 ± 5</td>
<td>Brittle</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.17</td>
<td>88 ± 8</td>
<td>88 ± 55</td>
<td>Brittle</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.07</td>
<td>262 ± 51</td>
<td>11 ± 5</td>
<td>Brittle</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.17</td>
<td>420 ± 36</td>
<td>4.3 ± 1.2</td>
<td>Increased pull-out</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.28</td>
<td>390 ± 21</td>
<td>0.6 ± 0.4</td>
<td>Pull-out</td>
</tr>
<tr>
<td>Carbon</td>
<td>&gt;0.5</td>
<td>352 ± 33</td>
<td>---</td>
<td>Pull-out</td>
</tr>
<tr>
<td>Nextel-440</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Uncoated</td>
<td>61 ± 35</td>
<td>76 ± 38</td>
<td>76 ± 38</td>
<td>Brittle</td>
</tr>
<tr>
<td>Carbon</td>
<td>0.4</td>
<td>172 ± 30</td>
<td>0.8 ± 0.3</td>
<td>High pull-out</td>
</tr>
</tbody>
</table>

*Calculated from weight gain.*
Fig. 1. Schematic of forced chemical vapor infiltration apparatus.

Fig. 2. Hot (top) surface temperature during infiltration vs flexural strength of specimens from top layer of the composites.

Fig. 3. Typical load-displacement curves from flexure strength measurements of SiC matrix composites containing Nicalon, FP, Nextel-440, and Tyranno fiber reinforcement. (T.D. indicates theoretical density.)
Fig. 4. Typical load-displacement curves and scanning electron microscope photographs of fracture surfaces of SiC matrix composites reinforced with (a) uncoated Nicalon and (b) Nicalon coated with 0.17 μm of silicon.
Fig. 5. Typical load displacement curves for SiC matrix composites reinforced with uncoated Nicalon fibers and Nicalon precoated with pyrolytic carbon to various thicknesses (t).

\[ T = 1473 \text{K} \]

\[ H_2 = 500 \text{cm}^3/\text{min} \]

\[ MTS = 50 \text{cm}^3/\text{min} \]

Fig. 6. Processing time vs theoretical density of the hot (top) surface and cool (bottom) surface as calculated from the one-dimensional model of forced chemical vapor infiltration. Also shown is a metallographic cross-section of a Nicalon preform infiltrated for 6 h under the conditions shown.

Fig. 7. Experiment vs model-predicted processing times.