

Fabrication of a Nicalon™ fiber/Si₃N₄-based ceramic-matrix composite by the polymer pyrolysis method

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A processing route for ceramic matrix composites is developed based upon polymer pyrolysis. Three types of Nicalon™ fiber woven fabrics,—i.e., uncoated, carbon-coated, and carbon/SiC-coated—are impregnated with a polysilazane solution. Thus-formed prepregs are then cut, laminated, pressed and fired to 1000 °C in a nitrogen atmosphere. Upon pyrolysis, polysilazane converts to a Si₃N₄-based ceramic matrix with ~60 wt% yield. The composites made with uncoated Nicalon™ fibers have poor flexural and tensile strength (103 and 19 MPa, respectively) and show brittle fracture behavior. That is due not only to the poor fiber-matrix interface but also to processing-induced fiber damage. For carbon and carbon/SiC-coated Nicalon™ fiber composites, the coating layers on the fiber surface manipulate the appropriate fiber-matrix interface and also protect the fibers from damage during polymer pyrolysis, so these composites exhibit higher flexural (250 and 274 MPa, respectively) and tensile (138 and 196 MPa, respectively) strength. Also, the load stress-deflection behavior of composites with two types of coated fibers cause noncatastrophic fracture. © 2000 Kluwer Academic Publishers

1. Introduction

Ceramic matrix composites (CMCs) are expected to play as important a role in high temperature applications as polymeric matrix composites do at low to medium temperature. During the past decade, significant advance has been made in the understanding of the mechanisms of fiber reinforcement and failure behavior of CMCs. However, the development of cost-effective processing techniques remains the key challenge.

Processing routes [1], such as hot-pressing [2], melt infiltration [3], slurry infiltration [4], chemical vapor infiltration (CVI) [5], gas-metal reaction [6], sol-gel [7], and polymer pyrolysis [8] are available for the fabrication of long fiber CMCs. Each fabrication technique has its advantages and disadvantage or limitation.

Polymer pyrolysis has been successfully used for fabrication of advanced fibers, such as carbon fiber, silicon carbide fiber and Si-C-N fiber. This technique is also suitable for producing matrices for CMCs, and is particularly attractive as it involves a pressureless pyrolysis process without high pressure sintering. Also, some techniques used in processing polymer-matrix composites, i.e., bag molding, resin transfer molding and fila-

ment winding can be combined with polymer pyrolysis to fabricate CMCs. Polysilazane with backbone Si-N is a desirable candidate for fabrication of Si₃N₄ ceramic matrix composites. The chemistry and pyrolytic characteristics of polysilazanes as ceramic precursors have been explored [9, 10]. The choice of polysilazane with proper molecular structure and good control of processing parameters can successfully lead to the fabrication of Si₃N₄-based composites.

The present paper reports about the fabrication and properties of Nicalon™ fiber-reinforced Si₃N₄-based ceramic matrix composites using the polymer pyrolysis method. The composites made with uncoated Nicalon™ fibers have poor flexural and tensile strength (103 and 19 MPa, respectively) and show brittle fracture behavior. That is due not only to the poor fiber-matrix interface but also to processing-induced fiber damage. For carbon and carbon/SiC-coated Nicalon™ fiber composites, the coating layers on the fiber surface manipulate the appropriate fiber-matrix interface and also protect the fibers from damage during polymer pyrolysis, so these composites exhibit higher flexural (250 and 274 MPa, respectively) and tensile (138 and

196 MPa, respectively) strength. Also, the load stress-deflection behavior of composites with two types of coated fibers cause noncatastrophic fracture.

2. Experimental procedures

2.1. Materials

Ceramic grade NicalonTM (manufactured by Nippon Carbon Company, Japan, and distributed by Dow Corning Corp. in USA) fabrics with three types of fiber surface treatments were used as the reinforcements in this experiment: (a) Uncoated fiber with polyvinylacetate sizing, 8-harness satin cloth. (b) Carbon-coated with polyvinylacetate sizing, 8-harness satin cloth. (c) Carbon/SiC-coated (pyrocarbon + SiC duplex coated), plain weave cloth. The Nicalon fiberTM is more oxidation resistant than carbon fiber; it remains stable above 1000 °C and retains 80% of strength at 1200 °C in air [11].

A polysilazane (SILACERAM NCP-200, Chisso Company, Japan) was used as the precursor for Si₃N₄-based ceramic matrix. This polysilazane provides the following desirable characteristics [12]: (i) good control of molecular weight at ~1300 g/mole, (ii) resistance to hydrolysis and long shelf life, and (iii) ease of handling.

2.2. Fabrication of composites

Polysilazane was dissolved in toluene solvent; subsequently, the 2-D woven SiC fabric was impregnated with the solution. The prepregs so formed were dried, cut, laminated, pressed, and fired to 1000 °C in a nitrogen environment for pyrolysis of the polymer. Since pyrolysis was accompanied by evolution of gaseous by-products, the composite was very porous after the first infiltration/pyrolysis cycle. Six to eight cycles of infiltration and pyrolysis were used for densification of the composites. The fabrication process is schematically shown in Fig. 1. Specimens of the dimensions 1200 mm (*l*) × 40 mm (*w*) × 3 mm (*t*) were made for testing and characterization.

2.3. Characterization of composites

The density of each composite was determined by dividing the weight of the composite by its volume, which was measured using Archimedes' method. For porous composites, the surface was greased before measuring the volume in order to prevent the filling up of the pores by the fluid.

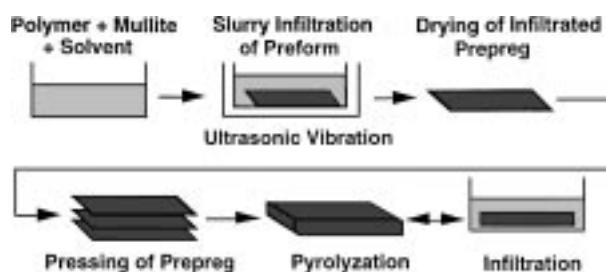


Figure 1 Schematic of the composite fabrication process.

Three-point flexural tests of composites were performed in an Instron 1125 machine. Specimens were cut into the dimensions of 5 (*w*) × 3 (*t*) × 40 (*l*) mm and tested with the span of 30 mm at the cross-head speed of 0.125 mm/min. At least eight samples were used for average values. Tensile test of composites were performed in Instron 8562 machine. Specimens were cut into the dimensions of 8 (*w*) × 3 (*t*) × 120 (*l*) mm and tested with the span of 60 mm at the cross-head speed of 0.125 mm/min. At least four samples were used for average values.

SEM observation was used to study the microstructures of composites.

3. Results and discussion

3.1. Density and porosity of composites

The properties of composites are shown in Table I and the improvement of composite densities are shown in Fig. 2. The composite with uncoated fibers has better fiber-matrix interfacial bonding. It also means that there is better compatibility between uncoated fiber and polysilazane or between uncoated fiber and matrix. And good compatibility between the fiber and matrix materials can result in a denser composite. After the same fabrication process, composites with uncoated fiber have higher density and lower porosity than those with coated fibers. Composites with the two different coated fibers exhibited similar properties.

3.2. Flexural properties of composites

The composite made with uncoated fibers has a flexural strength of 103 MPa and shows brittle fracture behavior. The composites made with carbon-coated fiber

TABLE I Properties of composites prepared with three different types of fibers

Fiber surface condition	V _f (%)	V _m (%)	V _p (%)	D _t (%)	ρ _c (g/cm ³)	ρ _t (g/cm ³)
Uncoated fiber	31.2	55.5	13.3	86.7	2.24	2.58
Carbon-coated fiber	29.7	50.9	19.4	80.6	2.08	2.58
Carbon/SiC coated fiber	30.3	51.1	18.6	81.4	2.10	2.58

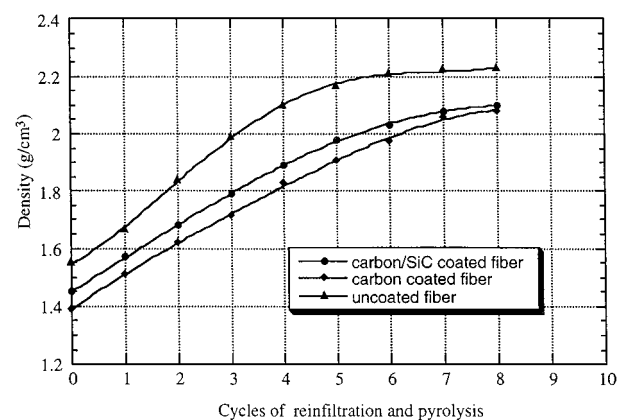


Figure 2 Improvement of density for composites with three different types of NicalonTM fibers after multiple re-infiltration and pyrolysis.

and carbon/SiC-coated fiber have much higher flexural strength, i.e., 250 and 274 MPa, respectively (Fig. 3 and Table II). Also, the stress-deflection behaviors of composites with two types of coated fiber show a non-catastrophic behavior (Fig. 3).

Substantial differences were observed from the fracture surfaces of these three composites. Brittle fracture surface was observed on the uncoated fiber composites (Fig. 4) and this is because of fiber damage during pyrolysis and a stronger fiber-matrix interface.

For both coated fiber composites, the coating provided protection for the fibers from chemical attack during the polymer pyrolysis process. This is shown in

TABLE II Flexural strength of composites with three different types of Nicalon™ fibers

Fiber surface condition	V_f (%)	V_p (%)	ρ_c (g/cm ³)	Flexural strength (MPa)
Uncoated fiber	31.2	13.3	2.24	103 ± 8
Carbon-coated fiber	29.7	19.4	2.08	250 ± 19
Carbon/SiC coated fiber	30.3	18.6	2.10	274 ± 17

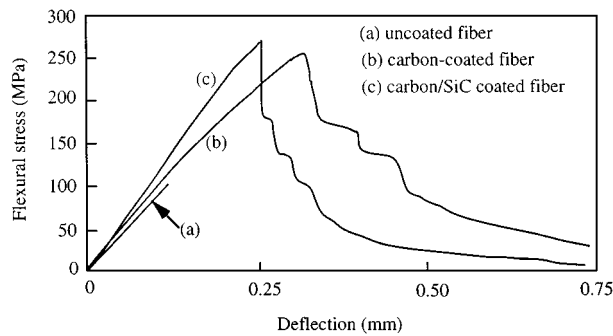


Figure 3 Stress-deflection curve of composites with three types of Nicalon™ fibers in three-point flexural test.

the experimental results described in Section 3.3. The carbon coating on the surface of Nicalon™ fibers also limits the fiber-matrix interface strength and prevents matrix cracks from penetrating neighboring fibers when the load is applied. Therefore, the coated fiber composites have much higher flexural strength and exhibited fiber pull-out on the fracture surfaces (Figs 5 and 6).

The flexural strength and modulus of the carbon/SiC-coated fiber composite are higher than those of the carbon-coated fiber composite. This is due to the SiC coating layer, which has higher strength and modulus than the amorphous matrix, and can be explained by the rule of mixtures. A comparison of Figs 4 and 5 showed that the carbon-coated fiber composite has longer fiber pull-out than the carbon/SiC-coated fiber composite. This is because the SiC coating layer absorbs a significant amount of energy and limits interfacial sliding, resulting in reduced fiber pull-out in the carbon/SiC fiber composite.

3.3. Tensile properties of composites

The tensile properties of composites made with uncoated, carbon-coated, and carbon/SiC-coated Nicalon™ fibers are compared in Table III and Fig. 7. The composites made with carbon-coated Nicalon™ fibers and carbon/SiC-coated Nicalon™ fibers have much higher tensile strength, i.e., 196

TABLE III Tensile properties of composites made with three different types of Nicalon™ fibers

Fiber surface condition	Tensile strength (MPa)	Tensile modulus (GPa)
Uncoated fiber	19 ± 5	47 ± 5
Carbon-coated fiber	138 ± 11	102 ± 9
Carbon/SiC-coated fiber	196 ± 13	133 ± 10

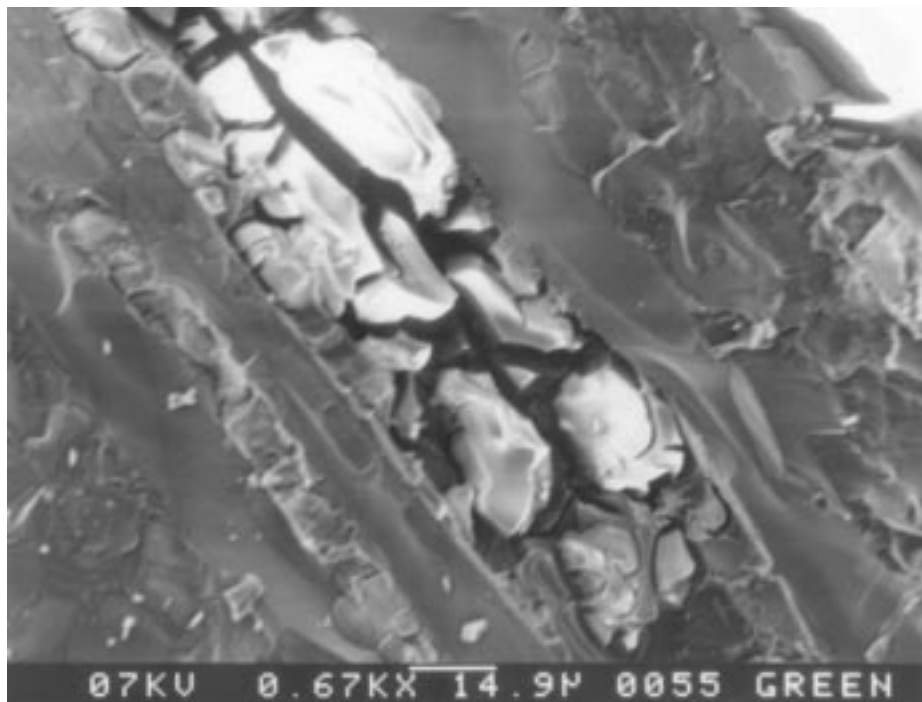


Figure 4 Fracture surface of uncoated fiber composite; no fiber pull-out was observed.

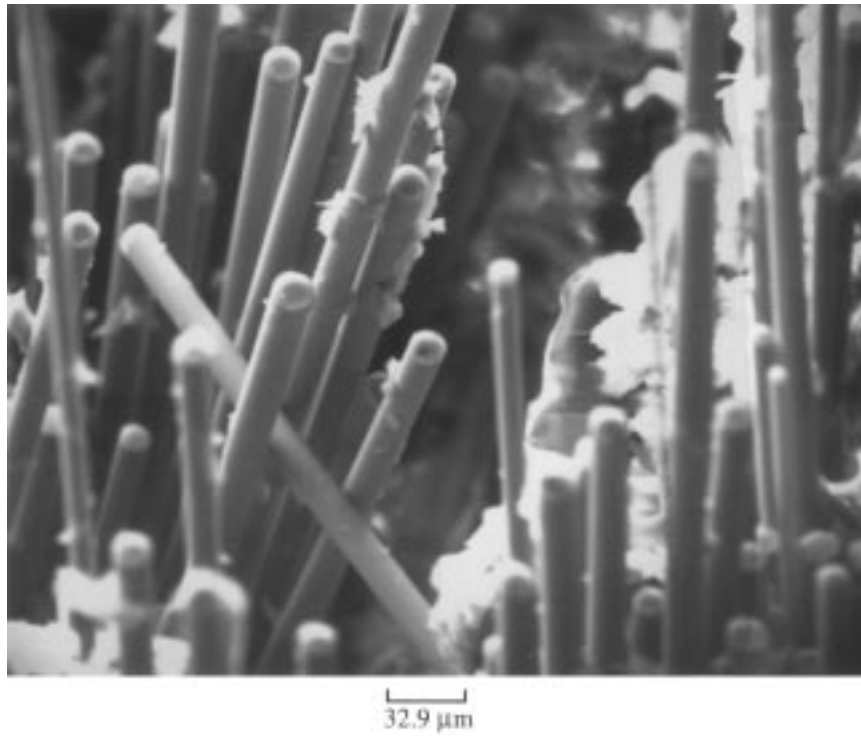


Figure 5 Fracture surface of carbon-coated fiber composite; fiber pull-out was observed (SEM, 300 ×).

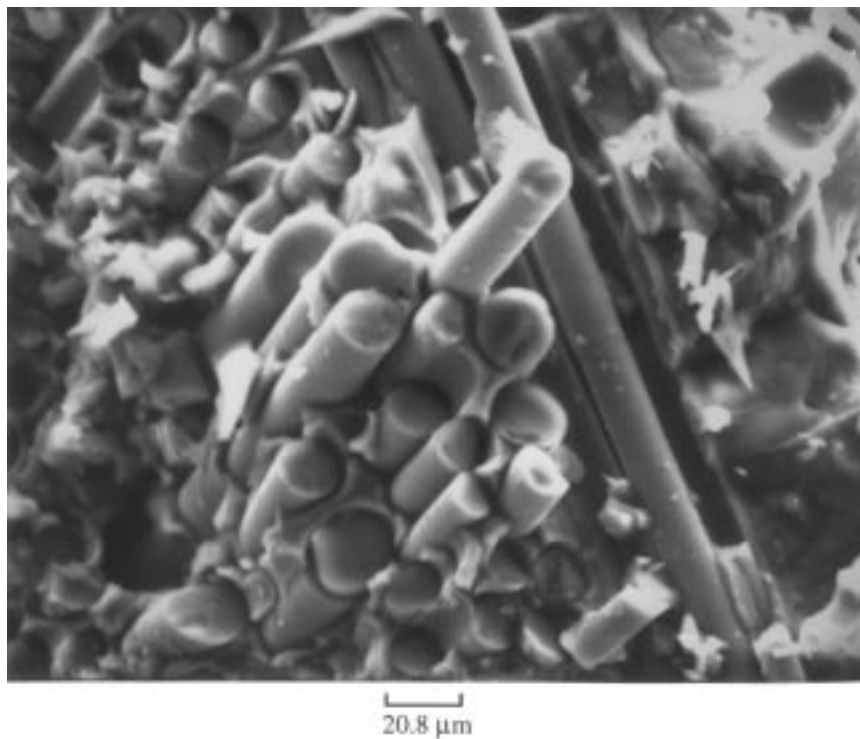


Figure 6 Fracture surface of carbon/SiC coated fiber composite; fiber pull-out was observed (SEM 480 ×).

and 138 MPa, respectively, than the uncoated fiber composite (19 MPa). Because of the fiber damage during pyrolysis, the uncoated fiber composite shows very low tensile strength.

The tensile strength and modulus of the carbon/SiC-coated fiber composite are higher than those of the carbon-coated fiber composite. Since the CVI SiC coating has a β -SiC crystalline [12], and higher strength and modulus than the polysilazane converted matrix. By the rule of mixtures, the introduction of the SiC

coating layer enhances the strength and modulus of the carbon/SiC-coated fiber composite.

3.4. Fiber strength before and after polymer pyrolysis

From the analysis of flexural and tensile properties, a substantial difference was found between uncoated and coated fiber composites. One possible reason for this difference is the fiber-matrix interface. For uncoated fiber composites, the fiber-matrix bonding is strong,

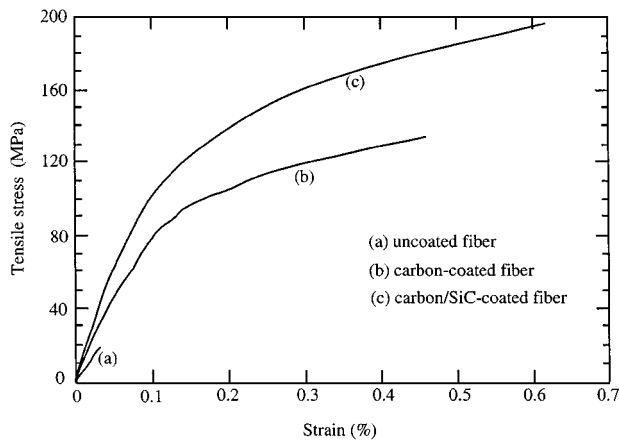


Figure 7 Tensile stress-strain behavior of composites made with three different types of Nicalon™ fibers.

then matrix cracking leads to fiber cracking and composites fail in a brittle and low-strength manner. For coated composites, the carbon coating layer around the Nicalon™ fiber can prevent the formation of a strong bond between the SiC fiber and ceramic matrix. So when a matrix crack reaches this layer, the stresses at the crack tip lead to fracture within this carbon layer along the fiber surface and thus blunt the matrix crack, resulting in a higher strength.

Another possible reason for the inferior properties of uncoated fiber composites is fiber damage caused by processing, especially during high-temperature polymer pyrolysis. In this section, an experiment was designed to investigate the strength of uncoated and carbon-coated fibers to enable comparison of fiber strength before and after polymer pyrolysis.

Fiber strands were used for the tensile strength test. Before testing, the fiber strands needed to be treated with a polymer binder to hold individual filaments together and prevent them from additional damage. The treatment of fiber strands with a polysilazane is shown in Fig. 8. Fiber strands were dipped in polysilazane solution in a glass pipette and passed through the tip hole (diameter of ~ 1 mm). Then the fiber strands were straightened and dried in a wooden supporter.

The tensile strength of uncoated and carbon-coated fibers under various treatments is shown in Fig. 9. For uncoated fibers, the strength of the starting fiber (2.45 GPa) is a little lower than the data provided by the manufacturer (2.8 GPa). That may be caused by some fiber damage during preparation process of the specimen for testing. If the fibers were heat treated at 1000°C for two hours, then there is another loss in tensile strength [13]. And unfortunately, the fiber impregnated with polysilazane and heat treated at 1000°C for two hours did not retain its strength—it was very fragile and broke at a low stress load. The fiber damage may be caused by chemical reactions between the fibers and the polysilazane polymer during high-temperature pyrolysis. The type of chemical reaction that occurred during processing is not clear, but residues of chloride compounds that come from preparing the polysilazane polymer materials may have reacted with the fibers and caused the damage.

For carbon-coated Nicalon™ fibers, even after heat treatment or polymer pyrolysis, the fibers retain more

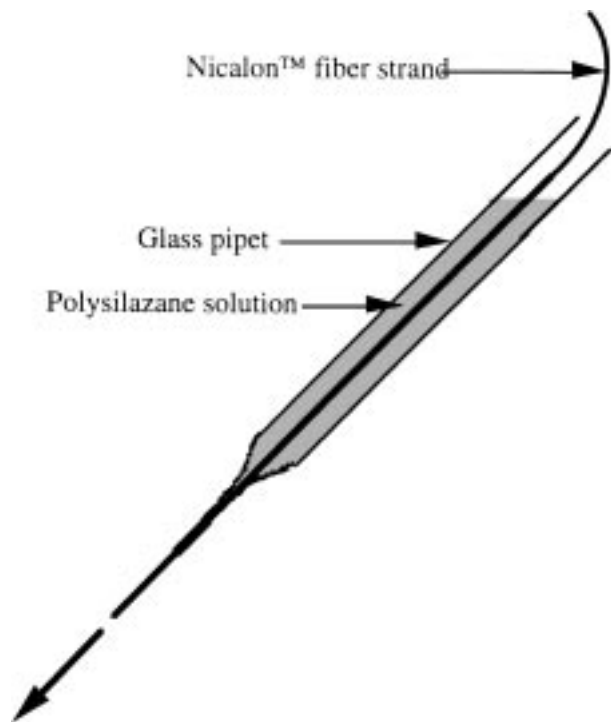


Figure 8 Treatment of fiber strand with polysilazane binder.

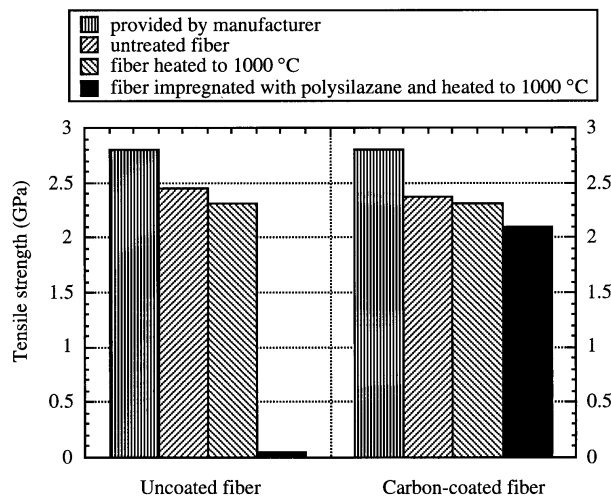


Figure 9 Comparison of tensile strength for uncoated and carbon-coated fibers, with different treatments.

than 80% of the original strength. This provides the evidence that Nicalon™ fibers need coating protection for application in the polymer pyrolysis process, in addition to the need of a coating for manipulating fiber-matrix interfaces.

The carbon/SiC-coated fibers were not used for tensile testing because of the difficulty in extracting fiber strands from fabric. But it is believed that this type of fiber also offers good protection from chemical reaction with polysilazane and can retain the fiber strength in the resulting composites.

3.5. Microstructures of composites with various types of fibers

To reduce the pores and densify the composite body, the composites were reimpregnated with polysilazane and pyrolyzed. The resulting composite microstructure after

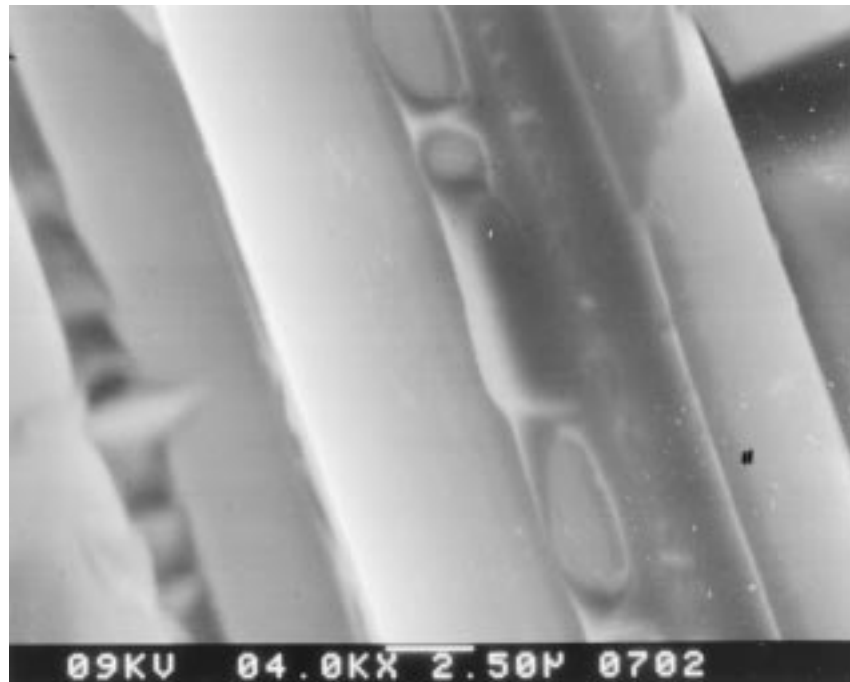


Figure 10 SEM micrograph of uncoated Nicalon™ fiber after the polymer pyrolysis.

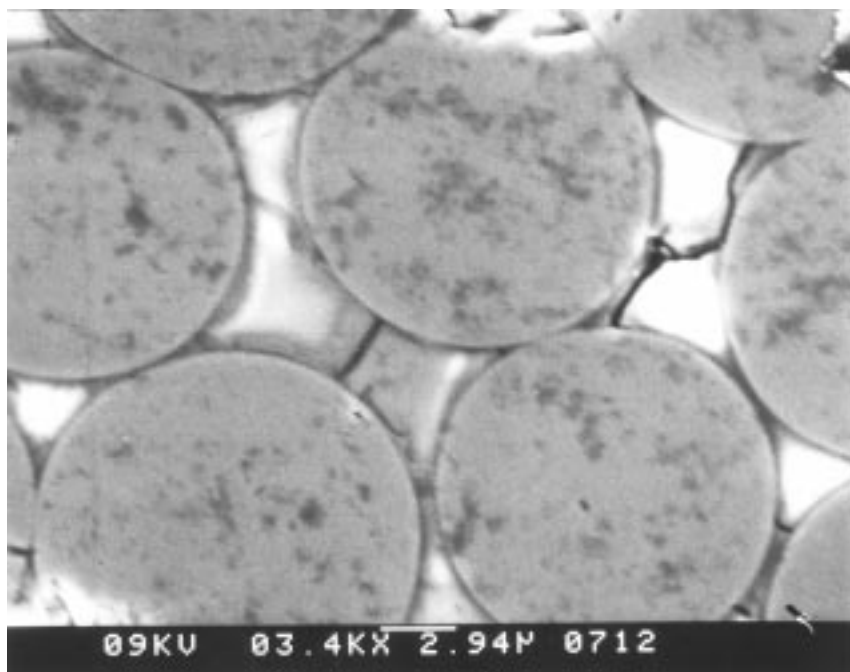


Figure 11 SEM micrograph of cross section and fiber-matrix interface for composite with uncoated fiber.

various cycles of reinfiltration and pyrolysis had been observed in our previous paper [14].

The flexural and tensile properties of composites with uncoated Nicalon™ fiber were very poor. This is mainly because damage to uncoated fibers during the polymer pyrolysis process renders the fibers incapable of playing the reinforcement roles. From SEM observation, even at very high magnification ($4000\times$, Fig. 10), damage could not be found on the fiber surface. But observation of a cross-section of the uncoated fibers shows unusual spots through all areas (Fig. 11). In comparison, the micrograph of coated fibers (Figs 12 and 13), though they may have microcracks that resulted

from sample polishing, show a smooth cross-section and no spots.

The spots of the uncoated fibers may indicate that some constituents of the fiber have been reacted by the invasion of polysilazane-based precursor. The integrity of the fiber has been damaged, resulting in a reduction in fiber strength. Further investigations of the detailed reactions are still needed.

The fiber-matrix interfaces of composites with three different types of Nicalon™ fibers can also be observed and compared from Figs 10 to 12. The uncoated fiber composite has a stronger fiber-matrix bonding interface. For the carbon-coated fiber composites, the carbon

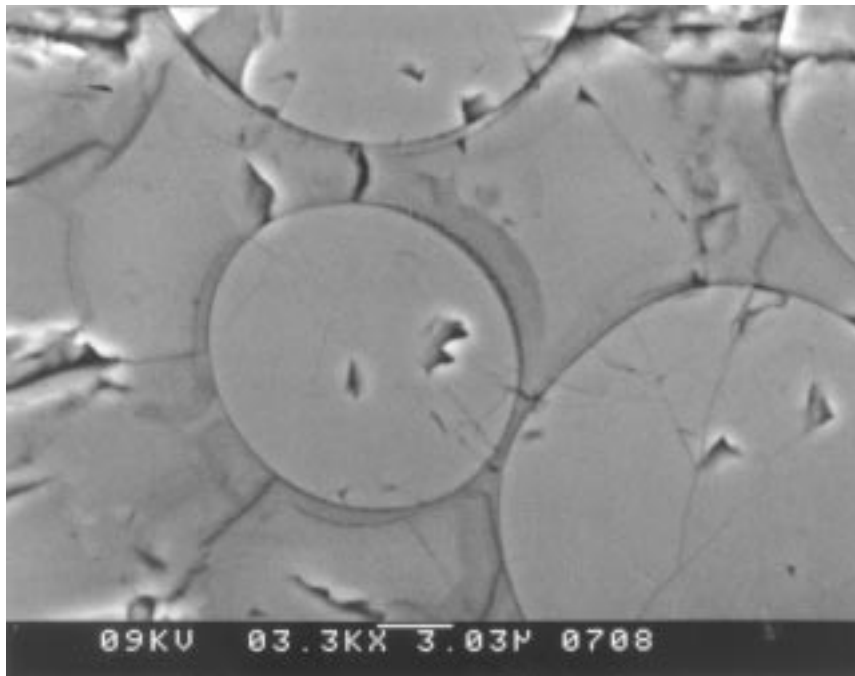


Figure 12 SEM micrograph of cross section and fiber-matrix interface for composite with carbon-coated fiber.

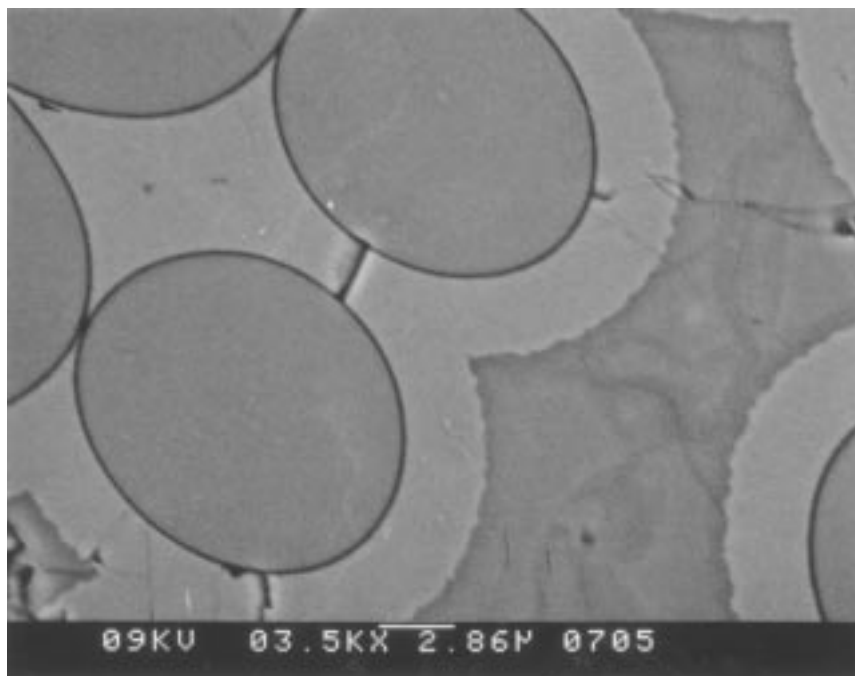


Figure 13 SEM micrograph of cross section and fiber-matrix interface for composite with carbon/SiC-coated fiber.

coated layer is thin (100–200 Angstroms, 0.01–0.02 μm), but the presence of the interface is clearly the controlling factor in determining composite strength and toughness. The carbon layer results in a weak fiber-matrix interface, which activates fiber pull-out and creates the toughening mechanism of composites.

The carbon/SiC coated fibers have about 3 μm thickness of SiC coating in addition to the pyrocarbon coating. The carbon/SiC coating layer can provide good protection on the NicalonTM fiber. Also, there is a good interface between the SiC coating and matrix material, so the toughening interface is still the inner pyrocarbon coating layer. The fiber pull-out on the fracture surface

of this kind of composite is consistent with this composite behavior.

4. Conclusions

The composites made with uncoated NicalonTM fibers have poor flexural and tensile strength (103 and 19 MPa, respectively) and show brittle fracture behavior. That is due not only to the poor fiber-matrix interface but also to processing-induced fiber damage. For carbon and carbon/SiC-coated NicalonTM fiber composites, the coating layers on the fiber surface manipulate the appropriate fiber-matrix interface and also protect the fibers

from damage during polymer pyrolysis, so these composites exhibit higher flexural (250 and 274 MPa, respectively) and tensile (138 and 196 MPa, respectively) strength. Also, the load stress-deflection behaviors of composites with two types of coated fiber show a non-catastrophic fracture behavior.

A specially designed experiment used to compare the strength of uncoated and coated Nicalon™ fiber strands under various treatment conditions provided the evidence that uncoated fibers suffer damage during polymer pyrolysis. From SEM observation, the cross-section of uncoated fibers showed unusual spots, further evidence of fiber damage.

The polymer pyrolysis method provides an efficient and economic route for processing ceramic matrix composites. The advantages of pressureless firing and suitability for net-shape manufacturing of multi-dimensionally reinforced composites make the polymer pyrolysis method very attractive to the ceramic composites industry.

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