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Improved thermomechanical stability of polymer-derived silicon carbide fibers by decaborane incorporation

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Decaborane was investigated as a precursor for boron-based densification aid to polymer-derived SiC fibers. By means of acid-base interaction, the infusibility of polycarbosilane-based polymers upon pyrolysis was enhanced significantly. The beneficial effect of decaborane toward improved thermomechanical stability took place when decaborane-doped SiC fibers were treated at 1800 °C. With the decaborane content at 2–4 wt %, the strength retention after the 1800 °C treatment was enhanced as high as 80%. Elastic modulus was improved as well, partly due to increased density and crystallinity. Improved densification by decaborane resulted in the fiber density as high as 2840 kg/m^3, which corresponds to 89% densification. Decaborane also increased the Weibull modulus after the 1800 °C treatment, indicating an enhancement in fiber reliability. © *2000 Kluwer Academic Publishers*

1. Introduction

Due to many superior properties [1], silicon carbide (SiC) fibers have been considered as one of the best reinforcing materials for the ceramic-matrix-composites in high temperature applications. Since Yajima's synthesis [2] of polycarbosilane (PCS) as precursor, polymer-derived SiC fibers have been extensively studied. Due to a carbon-rich stoichiometry as well as a low crystallinity, however, the thermomechanical stability of those fibers is good only below 1600 °C. One major mechanism of the thermal degradation of Nicalon^R and other polymer-derived SiC fibers has been reported to be the oxidation of silicon and carbon to form volatile CO and SiO products, which eventually develops a porous microstructure in fibers [3, 4]. Therefore, fibers should be provided with a proper densification mechanism which would work during heat-treatments at elevated temperatures.

Boron and its compounds are well-known densification aids for SiC materials. Boron precursor-based polymer chemistry has been extensively studied. A few phosphorus-containing polymers were synthesized and pyrolyzed to obtain ceramics [5]. The highest ceramic yield was attained with $-Ph_2POPPh_2-$ in the polymers, whose pyrolysis products were composed of boron, carbon, oxygen and phosphorus. According to chemical analysis results, the pyrolysis product has a large quantity of free carbon, residual oxygen and phosphorus [6]. Since the phosphorus-containing polymers resulted in undesirable ceramic products, the effort was shifted to amine-containing polymers [5, 7]. The structure of a typical polymer was $-[-B_{10}H_{12}$ diamine$-]_n-$, and upon pyrolysis in NH_3 resulted in mostly BN. The free carbon content was significantly reduced by pyrolysis in NH_3. Polyborasilazane was another polymer studied [8]. A black borosilicon carbonitride was formed when this polymer was pyrolyzed in argon, while a white borosilicon nitride was produced when pyrolyzed in NH_3.

Hexagonal-BN was produced when polyborazene was pyrolyzed at 1000 °C [9]. The same polymer was sprayed in aerosol droplets to produce fine powders [10]. The droplets were thermally decomposed at 1000 °C to make amorphous BN. Polymeric cyanoborane, $-[-CNBH_2-]_n-$, was used in a plasma-enhanced chemical vapor deposition of BN coating [11]. A severe contamination by paracyanogen was detected and the resulting BN was boron-deficient. BN was obtained from the pyrolysis of two oligomeric polysilaborazines [12]. Organic precursors have been added as sources of boron [13]. Carborane ($B_{10}H_{12}C_2$) and amino boranes have been used as precursors for B_4C on pyrolysis. Polyphenylbor ($[C_6H_5B]_n$) has been known as a precursor for boron and carbon. Pyridine-borane ($BH_3 : C_5H_5N$) was observed to give a suitable B : C ratio. A high homogeneity of boron and carbon was attained by the liquid-phase precipitation. High densification (99% at 2200 °C), retarded grain growth, and equiaxed fine grains (about 1.3 μm) were accomplished. None of the above materials, however, have been studied in conjunction with polymer-derived SiC fiber technology.

Novel PCS of high molecular weights (5000–10000) was synthesized by Toreki and his colleagues [14–16]. Instead of melt spinning of low molecular weight PCS to produce Nicalon^R fibers, solution spinning was used to fabricate SiC fibers [17] in this study. Candidate substances as boron precursors were evaluated using two criteria; homogeneity and ceramic yield. Since a typical fiber is less than 15 μm in diameter, a homogeneous mixing must be attained. The boron precursor, upon pyrolysis, must be converted to a corresponding boron compound with a reasonable ceramic yield. The precursor has to be uniformly mixed with polymer precursors for SiC fibers and they should be processed together without an appreciable phase segregation. Hence, the boron precursor should be solid at 25–80 °C, very soluble in toluene or other solvents along with PCS or PCS-based copolymers. From several potential substances, decaborane was selected in this study.

Decaborane is a colorless crystalline solid at room temperature (m.p. = 99.5 °C; b.p. = 231 °C). It has an intermediate volatility among boron hydrides [18]. It slowly evaporates at room temperature and crystallizes to needle shape. Decaborane is relatively stable with respect to air oxidation and does not decompose even when it is stored in air or oxygen at 50 to 60 °C. It has been reported that decaborane tends to decompose readily at temperatures over 150 °C [18]. B_{10}-cage has an open, 6-atom face which exhibits a boat conformation. Four of the six edges of the face are asymmetrically bridged by hydrogen atoms [19]. The unbridged B-B edges are significantly longer than the bridged B-B separations. The reaction of decaborane with weakly basic ligands such as acetonitrile was reported to take place as follows:

$$B_{10}H_{14} + 2CH_3CN \rightarrow B_{10}H_{12}(CH_3CN)_2 + H_2 \uparrow$$

In this reaction, the $B_{10}H_{14}$ cage is essentially reduced by losing two hydrogen atoms and acquiring two 2-electron donor ligands, corresponding to a net gain of two cluster electrons. The weakly bonded ligand is displaced by a ligand of greater nucleophilicity [19, 20]. The displacement reaction sequence in which a ligand on the right will displace that on the left can be expressed as below [20]:

$$\begin{aligned} R_2S = RCN < R_2NCN < R_2NCOR < R_3N < R_3P \\ = \text{pyridine} \end{aligned}$$

2. Experimental procedure

Two different kinds of polycarbosilane (PCS) were used as polymer precursor for SiC fibers in this study; commercial PCS of low molecular weight (MW = 1420–1450; Dow Corning X9-6348) and high molecular weight (5000–10000) PCS synthesized by Toreki [14–16]. Since the commercial PCS itself produces an extremely poor ceramic yield upon the 1000 °C pyrolysis, it was chemically crosslinked using a vinyl silazane monomer prior to fiber processing [21]. High MW PCS was synthesized from polymethylsilane (PMS: Huls) by pressure pyrolysis at 450 °C for 24 hours in an autoclave [14–16]. Polysilazane was added to the high MW PCS to improve the spinning processibility as well as the ceramic yield.

Decaborane was mixed with PCS-based polymer in toluene. Stirred mixture solutions were filtered using 0.45 μm PTFE filters, followed by the evaporation process to adjust the solution viscosity suitable for fiber spinning [21, 22]. Since the decaborane-doped polymer solution tended to turn hazy and extremely viscous when it was left longer than two hours, fiber spinning was performed immediately.

Spun polymeric fibers were pyrolyzed at 1000 °C to produce ceramic fibers. Some of pyrolyzed fibers were treated further in the temperature range 1300–1800 °C to examine the thermomechanical stability. The 1500 °C treatment was performed in a tube furnace (Lindberg GS) with argon flow at the rate of 3×10^{-5} m^3/min. On the other hand, the 1800 °C treatment was carried out using a batch furnace (Centorr) with argon flow. In each treatment, fibers were held for an hour at the peak temperature.

Material characterizations were performed via x-ray photoelectron spectroscopy (XPS; Perkin-Elmer 6000 series), scanning Auger microscopy (SAM; Perkin-Elmer Φ660), scanning electron microscopy (SEM; JEOL JSM-6400) and x-ray diffractometry (XRD; Philips APD 3720). Tensile properties of SiC fibers were measured using Instron^R (model 1123) based on ASTM D3379-75 [23]. A personal computer was connected to read and record the yield and the failure stresses accurately. The cross-head speed was 0.5 mm/min. Fiber density was measured by the sink-float method in accordance with ASTM D3800-79 [24]. Density values were determined by two methods; a microbalance and a pycnometer. Those two methods gave numbers in good agreement.

3. Results and discussion

3.1. Decaborane behavior

First, the decaborane effect on the pyrolysis yield was examined employing two specimen types, disks and powders, whose results are summarized in Table I. The decaborane content was fixed at 15 wt %. Apparently, decaborane incorporation brought a huge increase (approximately by 11% for each specimen) in the pyrolysis yield of PCS-based polymers. According to a separate experiment, the pyrolysis yield of decaborane itself was almost zero. Therefore, the improvement in the pyrolysis yield must be resulted from the chemical effect of decaborane.

No boron-containing crystalline phase, however, was detected in the XRD analysis. XPS analysis indicated

TABLE I Pyrolysis yields of PCS-based polymers

Specimen type	Pyrolysis yield (%)	
	Without decaborane	With decaborane (15 wt %)
powder	66.2 ± 1.2	77.5 ± 0.8
disk	69.7 ± 0.6	80.3 ± 1.1

that boron was detected on the surfaces of disk specimens at 4–6 atomic %. Decaborane reacts with a Lewis base to fill its open cage with electron-pair donating substance [19]. When electron-pair accepting decaborane molecules were in contact with electron-pair donating nitrogen atoms in silazane (either monomer or polysilazane), a strong acid-base interaction bound them together, which consequently resulted in an enhanced chemical crosslinking effect for increased pyrolysis yield.

3.2. Decaborane-incorporated SiC fibers

Fig. 1 illustrates the decaborane effect on the fiber tensile strength after 1500 °C and 1800 °C treatments. It seems that SiC fibers derived from high MW PCS-based polymers have substantially greater as-pyrolyzed strength than those from low MW PCS-based polymers. The strength of all fibers, even with decaborane, was greatly reduced to below 1.0 GPa after the 1500 °C treatment. Hence, there was no positive effect of decaborane on strength at the 1500 °C treatment. In contrast, the decaborane incorporation was in effect when fibers were treated at 1800 °C. After the 1800 °C treatment, the fiber strength with decaborane bounced back to ∼1.5 GPa whereas fibers without decaborane became extremely fragile.

This trend, a greater fiber strength after the 1800 °C treatment than the 1500 °C treatment, was observed consistently throughout our study. This is supposedly the principal effect of decaborane incorporation. Decaborane would not play a beneficial role toward densification during the 1500 °C treatment because the temperature is too low. Instead, oxidative degradation reactions would occur between residual oxygen and other elements, such as carbon and silicon:

$$\mathrm{SiC} + 2\mathrm{O} \rightarrow \mathrm{SiO}\uparrow + \mathrm{CO}\uparrow\ @{\sim}1500\,^{\circ}\mathrm{C}$$

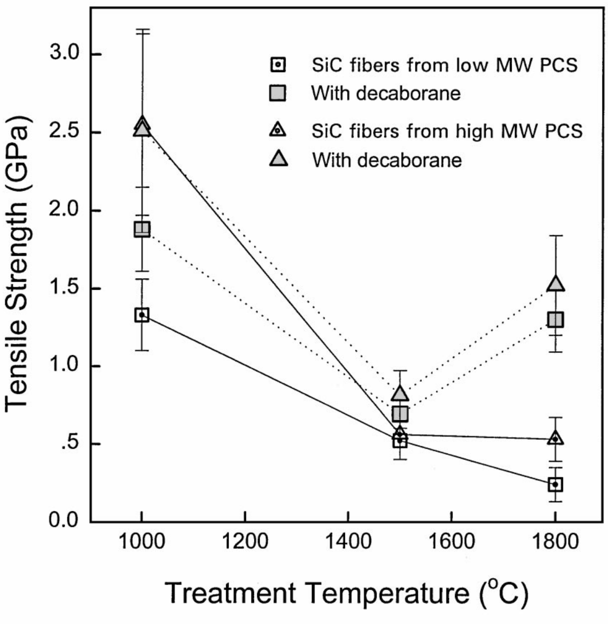


Figure 1 Effect of decaborane (at 3.2 wt %) on fiber strength after treatments at 1500 and 1800 °C.

TABLE II Effect of decaborane content on the tensile properties of a typical SiC fiber batch: As-pyrolyzed and after the 1800 °C treatments

Decaborane content (wt %)	Avg. fiber diameter (micron)	Tensile strength (GPa)	Elastic modulus (GPa)	Rupture strain (10^{-3})
< As-pyrolyzed fibers >				
0	14.7	2.55 ± 0.61	154 ± 24	16.6 ± 3.3
1.1	19.0	2.16 ± 0.41	182 ± 8	11.9 ± 2.3
3.2	17.9	2.51 ± 0.65	187 ± 7	13.4 ± 3.4
7.6	17.3	1.90 ± 0.41	207 ± 9	9.1 ± 1.8
< After the 1800 °C treatment >				
0	17.1	0.53 ± 0.20	119 ± 34	4.7 ± 0.8
1.1	19.0	0.68 ± 0.22	211 ± 20	3.2 ± 0.8
3.2	18.0	1.52 ± 0.32	209 ± 10	7.2 ± 1.4
7.6	16.7	1.39 ± 0.22	212 ± 14	6.6 ± 1.2

The above reaction would create tiny pores and thus microporous structure in fibers, which would be detrimental to fiber strength. In contrast, decaborane played an active role during the 1800 °C treatment not only in the densification but also in the crystallization in SiC fibers.

Table II summarizes the effect of initial decaborane content on the tensile properties of SiC fibers in a typical case; as-pyrolyzed and after the 1800 °C treatment. After the 1800 °C treatment, SiC fibers without decaborane not only became fragile with extremely low strength but also showed greatly reduced elastic modulus. Up to 1.1 wt %, no appreciable improvement by decaborane in the thermomechanical stability was observed. When its content was 3.2 wt %, the strength retention after the 1800°C treatment was remarkably improved by more than 60% with an improvement as high as 80% recorded for one sample. A further increase in decaborane content over 3.2 wt % did not result in a further enhancement in thermomechanical properties of fibers. In fact, a decaborane content over 7.6 wt % caused sticking between individual fibers. Therefore, the content near 3.2 wt % seems to be suitable for decaborane-doped SiC fibers.

Another beneficial effect of decaborane seems to occur to the fiber elastic modulus. As shown in Table II, the elastic moduli of fibers doped with decaborane at 1.1 and 3.2 wt % were greater after the 1800 °C treatment than those as pyrolyzed. The significant reduction in fiber strength after the 1800 °C treatment should be associated with a large decrease in rupture strain. In other words, fibers became much more brittle probably due to defects and grain-coarsening in microstructure during treatments at elevated temperatures.

Fig. 2 summarizes the change in strength and modulus retention of SiC fibers after the 1800 °C treatment as a function of the decaborane content. Overall, both retention ratios gradually increased with increasing decaborane content. Those ratios seemingly leveled off in the 2–7 wt % of decaborane content range. Considering the rupture strain combined with strength, the optimal decaborane content seems to be 2–4 wt %. Decaborane is believed to have two effects on SiC fibers; a positive effect to improve densification and a negative one to exist as an impurity. The optimal decaborane

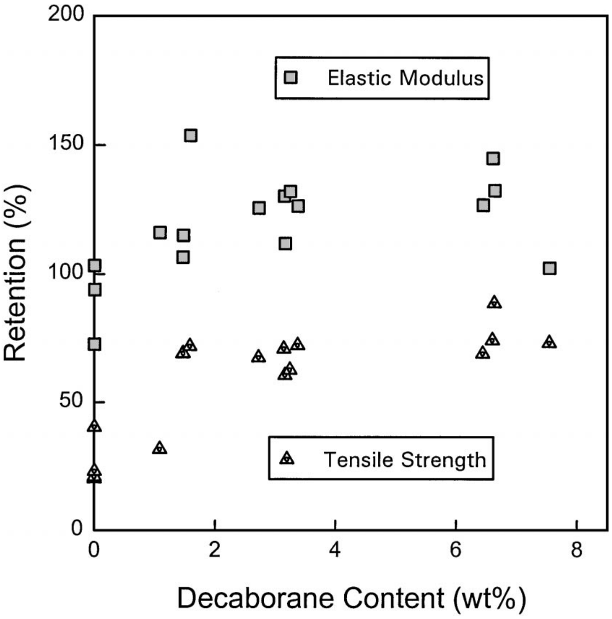


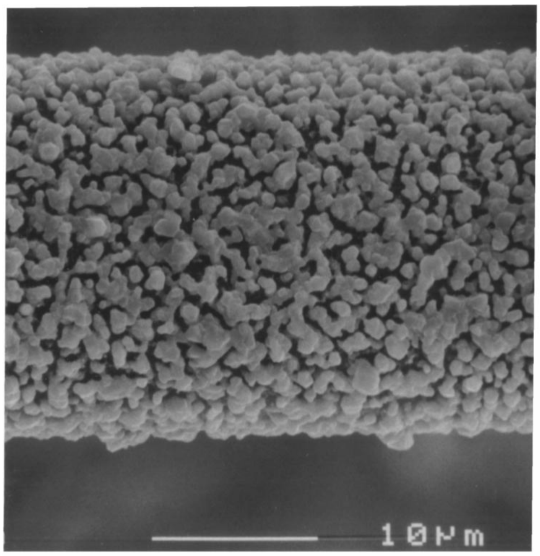
Figure 2 Effect of decaborane content on strength and modulus retention after the 1800 °C treatment.

content should be determined by a trade-off between those two effects under given conditions.

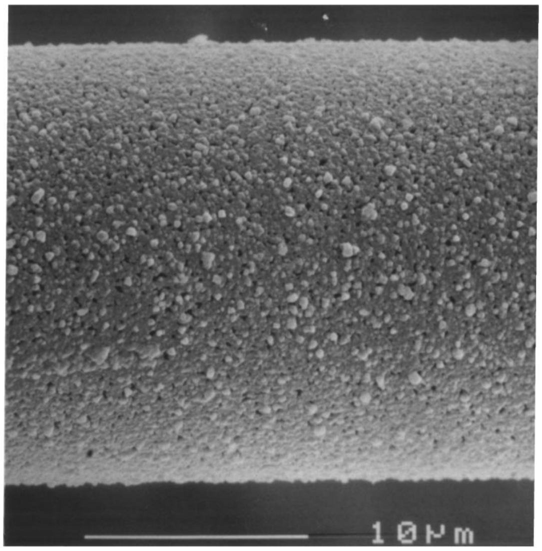
Fig. 3 shows typical SEM surface micrographs of SiC fibers with various decaborane contents after the 1800 °C treatment. Fibers without decaborane had extremely rough surface on which many particles of approximately one micron in diameter were closely attached. Those particles are presumably SiC crystallites that were grown excessively during the 1800 °C treatment. The fiber morphology after the 1800 °C treatment was gradually improved as the decaborane content was increased. Fibers with 3.2 wt % decaborane retained their smooth surface even after the 1800 °C treatment. In most cases, the fracture of ceramic fibers is initiated from cracks and defects on the surface [25]. In this sense, the improved mechanical properties of SiC fibers with decaborane after the 1800 °C treatment were largely attributed to the surface densification effect.

In terms of mechanical properties, the decaborane effect was apparent after the 1800 °C treatment, but not at all as-pyrolyzed or after the 1500 °C treatment. A similar effect was observed in XRD analysis. When the decaborane was doped at 3.2 wt % to SiC fibers, there was no appreciable difference in XRD patterns either as pyrolyzed or after the 1500 °C treatment. As shown in Fig. 4, however, the decaborane incorporation had a substantial effect on the XRD pattern after the 1800 °C treatment. Intensity of diffraction peaks corresponding to crystalline β-SiC with decaborane was much greater than that without decaborane. Since the peak area (below each peak; in this analysis, peak for (111) was selected) is supposedly proportional to the amount of crystalline phases, it is clear that the decaborane enhances the crystallization process of β-SiC during the 1800 °C treatment.

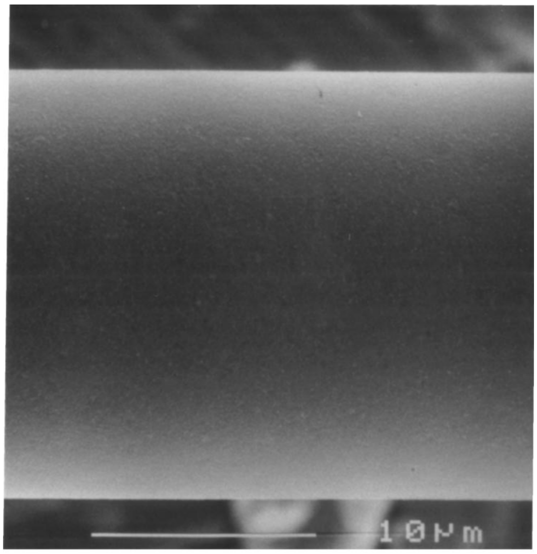
Two other effects of decaborane were observed. First, decaborane seems to suppress the transition of β-SiC to



No decaborane



1.1 wt % decaborane



3.2 wt % decaborane

Figure 3 Effect of decaborane content on fiber's surface morphology after the 1800 °C treatments.

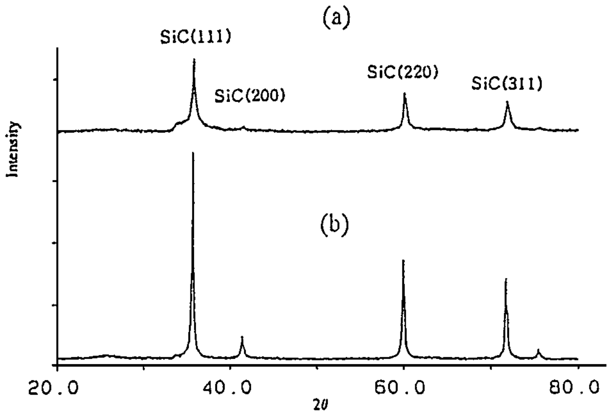


Figure 4 Effect of decaborane on typical XRD patterns of SiC fibers after the 1800 °C treatment: (a) without decaborane and (b) with decaborane at 3.2 wt %.

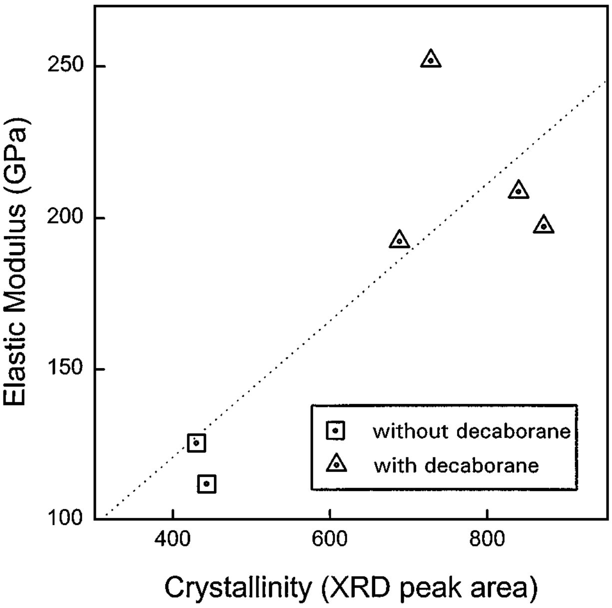


Figure 5 Plot of average elastic modulus of SiC fibers versus crystallinity (peak area).

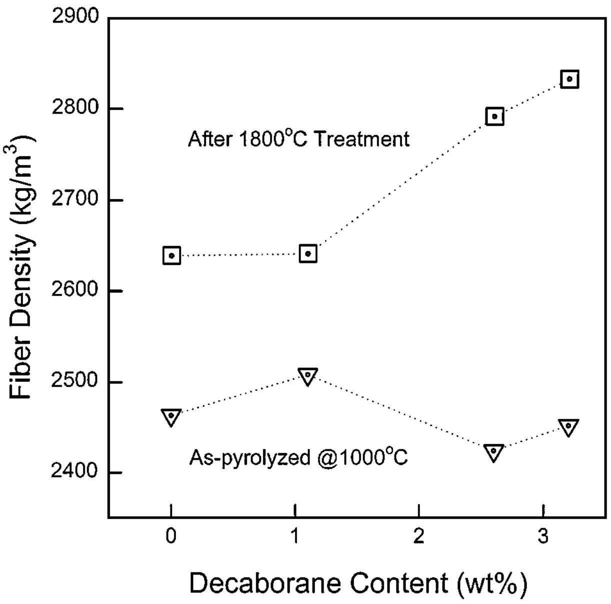


Figure 6 Plots of fiber density versus decaborane content: as-pyrolyzed and after the 1800 °C treatment.

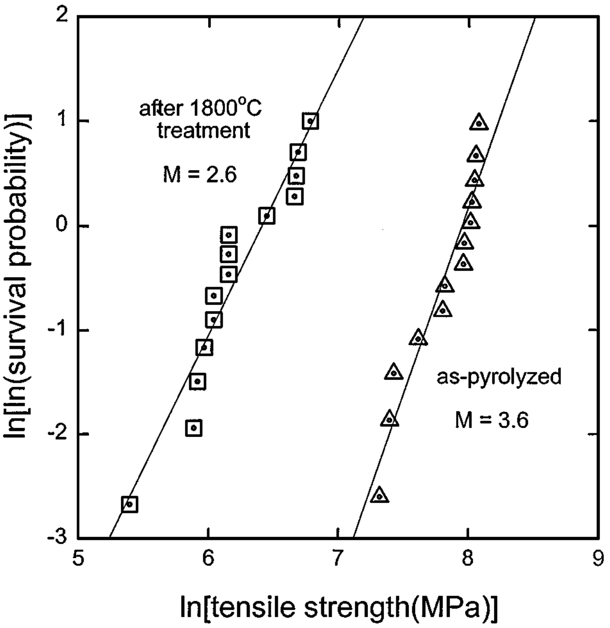


Figure 7 A typical Weibull plot for SiC fibers without decaborane: as-pyrolyzed and after the 1800 °C treatment.

α-SiC during the 1800 °C treatment. α-SiC, thermodynamically favorable crystalline form over 1600 °C and characterized by a diffraction peak at $2\theta = 34.2°$, was hardly detectable in XRD spectra. Secondly, decaborane incorporation resulted in an increase in the grain size, which was confirmed by a reduction in full-width-half-maximum (FWHM) of diffraction peaks.

Fig. 5 illustrates the plot of elastic modulus versus XRD peak area. A rough correlation can be made that higher crystallinity leads to greater modulus. A study of microstructure change in SiC fibers by decaborane is needed for further analysis. The measured grain size of decaborane-doped SiC fibers after the 1800 °C treatment (based on Scherrer's formula) [26] was 25–30 nm, smaller than that of boron-doped SiC fibers (~500 nm) reported in literature [27].

The decaborane effect on fiber density after the 1800 °C treatment is summarized in Fig. 6. The as-pyrolyzed fibers have the density range 2430–2510 kg/m^3. The density was slightly increased to 2620 kg/m^3 after the 1800 °C treatment, even without decaborane. Incorporating decaborane at a low level such as 1.1 wt % was not effective in improving the density after the 1800 °C treatment. This result is in good agreement with tensile properties shown in Table II. When SiC fibers were prepared with decaborane of 3.2 wt %, the density reached 2840 kg/m^3 after the 1800 °C treatment, which corresponds to approximately 89% densification.

Finally, Weibull analysis was performed to examine the decaborane effect on fiber reliability [28]. Following is the expression utilized to calculate the survival probability $P_s(V)$:

$$P_s(V) = \frac{1-i}{(N+1)} \quad i = \text{strength rank}; 1, 2, \ldots, N,$$

where N = total number of tested specimens (11–20). Figs 7 and 8 show typical Weibull plots of SiC fibers.

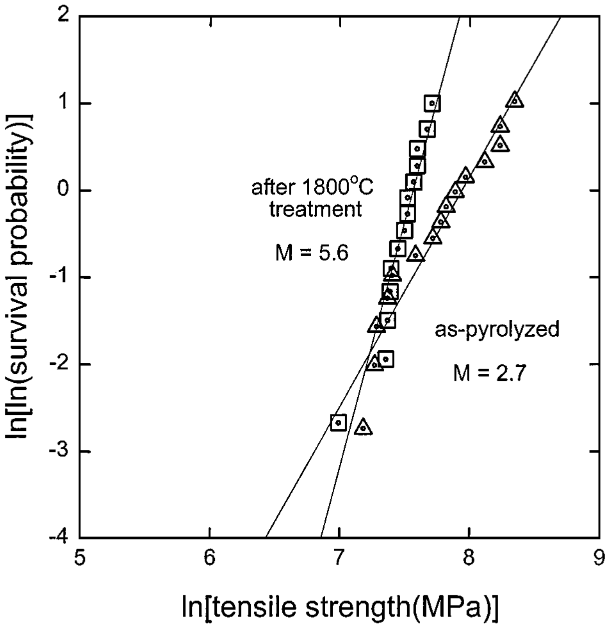


Figure 8 A typical Weibull plot for SiC fibers with decaborane (3.2 wt %): as-pyrolyzed and after the 1800 °C treatment.

In Fig. 7, the Weibull modulus (referred to as M) of SiC fibers without decaborane was decreased from 3.6 to 2.6 by the 1800 °C treatment. On the other hand, as shown in Fig. 8, decaborane brought about an huge increase (from 2.7 to 5.6) in the Weibull modulus after the 1800 °C treatment. Hence, the reliability of SiC fibers after the 1800 °C treatment was substantially enhanced by decaborane incorporation.

As mentioned previously, the mechanical properties of SiC fibers strongly rely on the surface morphology. Provided that the decaborane works on surface densification, it would be more desirable to have a greater ceramic yield of decaborane when boron-doped polymer fibers are pyrolyzed. According to a reference [29], the decomposition reaction of decaborane can be suggested as below. If free carbon is available nearby, there should be a greater chance for the following reaction to take place and produce boron carbides:

$$B_{10}H_{14} \rightarrow 10B + 7H_2 @ {\sim}300\,^\circ\mathrm{C}$$

$$4B + C(\text{excess in SiC}) \rightarrow B_4C$$

Therefore, a fast heating might help above reactions to occur with improved yield. Nevertheless, the heating rate as high as 15 °C/min during the 1000 °C pyrolysis did not reveal a noticeable enhancement in terms of surface morphology.

4. Conclusion

1) A strong acid-base interaction between decaborane and nitrogen in silazane improved the infusibility of polymers and thus the ceramic yield during pyrolysis at 1000 °C.

2) The beneficial effect of decaborane on the thermomechanical stability of SiC fibers showed up after the 1800 °C treatment. Also, its content has to be in the range of 2–4 wt % in terms of initial composition. With decaborane, SiC fibers retained smooth surface even after the 1800 °C treatment.

3) Tensile properties of SiC fibers after the 1800 °C treatment were greatly improved by decaborane incorporation. The fiber modulus became even higher after the 1800 °C treatment than that as pyrolyzed. Decaborane was effective in densification to increase the fiber density to a great extent after the 1800 °C treatment. A fiber density as high as 2840 kg/m^3 was attained, which corresponds to 89% densification.

4) According to Weibull analysis results, the reliability of polymer-derived SiC fibers after the 1800 °C treatment can be substantially enhanced by decaborane incorporation.

5) It is believed that the fracture of decaborane-incorporated SiC fibers was initiated by cracks or defects on the fiber surfaces. A method to keep the boron content sufficient on fiber surfaces during the pyrolysis must be developed.

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