JOURNAL OF MATERIALS SCIENCE **36** (2001) 357–362

Fine silicon carbide fibers synthesized from polycarbosilane-polyvinylsilane polymer blend using electron beam curing

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A fine SiC fiber is synthesized from a polymer blend of polycarbosilane (PCS) and polyvinylsilane (PVS) with electron beam curing under vacuum. The obtained SiC fiber from the PCS-PVS blend polymer has smaller average diameter of 8.5 μm than that of 11.8 μm from PCS, and shows higher average tensile strength of 3.2 GPa than that of 2.8 GPa from PCS after heat treatment at 1673 K in Ar gas atmosphere. However, the SiC fiber from the polymer blend decreases in tensile strength after heat treatment above 1773 K due to β-SiC crystal growth near the fiber surface, because of a small amount of oxygen incorporated in the fiber. © *2001 Kluwer Academic Publishers*

1. Introduction

Ceramic fibers with high performance are required for development of ceramic matrix composites (CMCs). In order to weave ceramic fibers into 2-dimension or 3-dimension fabrics for the reinforcement of CMCs, it is important to fabricate finer fibers that have higher tensile strength and flexibility. As several kinds of ceramic fibers are studied for CMCs, silicon carbide (SiC) fiber is one of the likeliest candidates [1–4], because of its promise for finer ceramic fibers and resistance at high temperature.

SiC fibers have been mainly fabricated by pyrolysis of organosilicon polymer fibers, such as polycarbosilane (PCS) [5, 6]. To synthesize a finer SiC fiber, it is necessary to melt-spin the polymers into finer fibers and then to pyrolyze them. To obtain the finer polymer fibers, it is important to control the viscosity of organosilicon polymers and to lower the melt-spinning temperature of the polymers. These characteristic polymers are obtained by blending polyvinylsilane (PVS) [7, 8], a viscous liquid, with PCS, a solid at ambient temperature [9–11].

It is necessary to cure the polymer fibers before the pyrolysis in order to prevent the polymer fibers from melting during the pyrolysis process. Thermal oxidation curing, a conventional method, is not suitable for curing of the polymer fibers, because a large amount of oxygen atoms is incorporated in the fibers during the curing process. Oxygen atoms in SiC fibers weaken the tensile strength of the fibers at temperature above 1500 K [11–17]. Radiation curing of the PCS polymer fibers under vacuum or an atmosphere without oxygen has been developed [18–20]. SiC fiber synthesized with this curing method has excellent thermal resistance up to 2000 K, because of extremely low oxygen content in the fiber [21–24]. However, the diameter and tensile strength of the SiC fiber obtained until now are 14 μm and 2.8 GPa, respectively, at most. In the work reported here we attempted to fabricate a finer and stronger SiC fiber from the PCS-PVS polymer blend.

In this paper, a SiC fiber is synthesized from the polymer blend with the curing by electron beam (EB) irradiation under vacuum. The properties of the SiC fibers, such as a tensile strength and a thermal resistance, are measured, analyzed, and compared with a SiC fiber from PCS, used as a reference.

2. Experimental procedure

2.1. Preparation of polymer blend fiber

Polycarbosilane (PCS), supplied by Shin-Etsu Chemicals Co., Ltd., is a solid polymer at ambient temperature, and has a number average molecular weight of 2.0×10^3. Polyvinylsilane (PVS), supplied by Mitsui Chemicals, Inc., is a viscous liquid polymer, and has a number average molecular weight of

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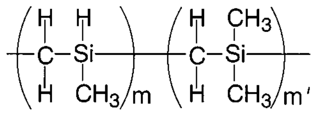
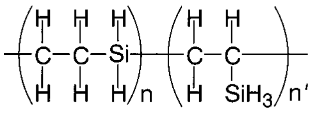


$$-\left(\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{H}{Si}}\right)_m\left(\underset{H}{\overset{H}{C}}-\underset{CH_3}{\overset{CH_3}{Si}}\right)_{m'}-$$

(a) Polycarbosilane (PCS)



$$-\left(\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{Si}}\right)_n\left(\underset{H}{\overset{H}{C}}-\underset{SiH_3}{\overset{H}{C}}\right)_{n'}-$$

(b) Polyvinylsilane (PVS)

Figure 1 Chemical formulas of organosilicon polymers.

9.6×10^2 [7, 8]. These chemical formulas are shown in Fig. 1. PVS contains no double bonds in the structure, and is highly rich in Si-H bonds as compared with PCS.

PCS-PVS polymer blend was prepared by freeze-drying of the benzene-organosilicon polymer solution under vacuum. PVS content in the polymer blend is fixed at 20 wt% to PCS from our previous experiment [11]. This polymer blend is abbreviated as "PCS-20%PVS." PCS-20%PVS polymer is a white powder at ambient temperature, and was melt-spun as following. The polymer blend was placed into a glass tube whose bottom is elongated to wedge-shape with a sharp tip, and heated to a spinning temperature of about 490 K after replacement of the atmosphere in the tube with Ar gas. After melting of the polymer blend, the tip of the glass tube was broken to make a spinneret whose diameter was about 0.5 mm. An Ar gas pressure, controlled slightly above 1 atm, extruded the melting polymer blend through the spinneret in air. PCS-20%PVS fiber was continuously wound on a rotating drum. As a reference, PCS fiber was also prepared at the spinning temperature of about 600 K.

2.2. Preparation of SiC fiber

The as-spun polymer fibers of PCS-20%PVS and PCS were placed into a quartz tube, and then the tube was evacuated. The fibers in the tube were irradiated with the doses of 5, 10, 15, and 20 MGy by 2 MeV electron beam (EB). During the irradiation, the tubes were cooled with water to prevent any temperature increment. After the irradiation, the fibers were heated at 773 K for 1.8 ks without taking them out from the tube to quench active species produced by the irradiation, because these active species are easy to react with oxygen in air [25].

The cured fiber means the polymer fiber irradiated by EB and subsequently heated at 773 K. To convert into SiC fibers, the cured fibers were pyrolyzed at 1273 K for 3.6 ks in Ar gas atmosphere. The heating rate to 1273 K was 5.6×10^{-2} K/s.

To investigate heat resistance of the SiC fibers obtained from PCS-20%PVS and PCS polymer fibers, the SiC fibers with the curing dose of 15 MGy were heat-treated in Ar gas atmosphere as following: a graphite crucible containing the SiC fibers was rapidly placed into a furnace preheated at an appointed temperature ranging from 1473 to 1773 K, and held for 3.6 ks.

2.3. Measurements and analyses of SiC fiber

The SiC fibers were observed by scanning electron microscopy (SEM: JSM-T20, JEOL). The tensile strength of the SiC fibers were measured at ambient temperature using a tensilon type machine (Tensilon, Toyo Measuring Instruments) with a gauge length of 10 mm and a crosshead speed of 3.3×10^{-2} mm/s. The average tensile strength was obtained by measuring 20 specimens.

The gases evolved from the SiC fibers were measured as following. An alumina tube containing the SiC fibers was evacuated, heated up to 1373 K with the heating rate of 3.3×10^{-2} K/s, and held for 1.8 ks at 1373 K. The gases accumulated in the tube were measured by gas chromatograph (Gas Chromatograph 163, Hitachi), which is equipped with Molecular Sieve 5A as a column, thermal conductivity detector (TCD) as a detector, and He gas as a carrier gas with flow rate of 0.5×10^{-7} m^3/s. After the measurement of evolved gases, the tube was evacuated again, and heated up to 100 K higher (1473 K) than the previous temperature (1373 K). The heating rate was 6.7×10^{-2} K/s up to the previous temperature and was slowed down to 3.3×10^{-2} K/s from the previous temperature to the higher temperature. The accumulated gases were then measured by the same method. This step was repeated every 100 K up to 1873 K.

Auger electron spectroscopy (AES) of the SiC fibers was measured with an AES microanalyzer (670xi, PHI) with an Ar^+ sputtering gun. The spot size of the measurement was about 1 μm. The intensities of Auger electron peaks as a function of depth from the fiber surface were recorded, and the relative concentrations of carbon, silicon, and oxygen atoms were analyzed using the sputtering rate reference as SiO_2.

3. Results and discussion

3.1. Synthesis of SiC fibers from PCS-PVS polymer blend

By blending 20 wt% of polyvinylsilane (PVS) with polycarbosilane (PCS), the softening temperature of the polymer blend becomes about 390 K, which is 110 K lower than that of 500 K for PCS, therefore, the polymer blend can be melt-spun at a lower temperature.

The average diameters of as-spun PCS-20%PVS (PCS blended with 20 wt% of PVS) and PCS polymer fibers obtained by the melt-spinning were 11.1 and 19.4 μm, respectively. In our previous experiment [11], the average diameters of PCS-20%PVS and PCS fibers were 15.0 and 26.7 μm, respectively. The diameter of PCS-20%PVS fiber is about half in comparison with that of PCS fiber, because the blend polymer is wound continuously at high winding speed in the spinning process due to its lower softening temperature, i.e., the polymer changes slowly from melting state to solid state in ambient atmosphere. In this experiment, polymer fiber could not be obtained from the polymer blends which contain over 30 wt% PVS, because the fibers from these polymer blends with high content of PVS stuck to each other on the rotating drum.

Fig. 2 shows yields of the SiC ceramic fibers obtained from PCS-20%PVS and PCS polymer fibers by

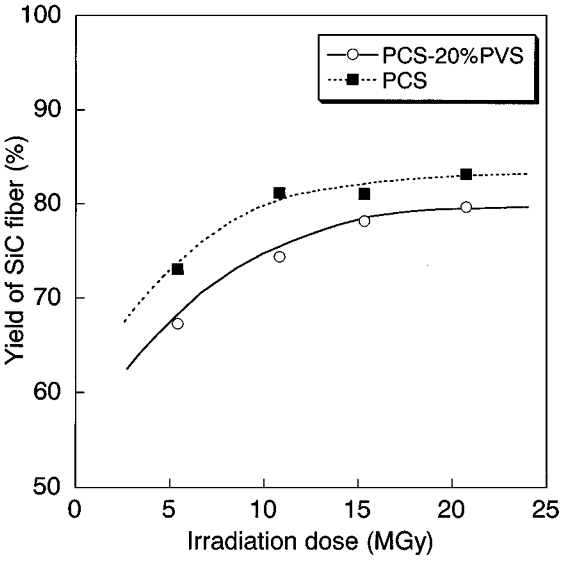


Figure 2 Relationship between curing dose and yield of SiC fibers obtained by pyrolysis subsequent to EB curing. Yield: weight ratio of ceramic fiber to as-spun polymer fiber; Pyrolysis: 1273 K for 3.6 ks in Ar gas atmosphere.

pyrolysis at 1273 K subsequent to electron beam curing. The yield is estimated by weight ratio of ceramic fiber to as-spun polymer fiber. Whereas the yields of the SiC fibers from both polymer fibers increase with increasing in the dose, the yield is almost saturated at about 78% for PCS-20%PVS above the dose of 15 MGy, and at about 83% for PCS above 10 MGy. Higher dose leads to more sufficient crosslinking of polymers in the fibers. The yield from PCS-20%PVS is about 5% lower than that from PCS. This is expected because the lower molecular weight components in PVS are decomposed and evaporated during the curing and the pyrolysis processes. In this paper, both the polymer fibers irradiated with the dose of 15 MGy are used for the following experiments.

Fig. 3 shows the diameter distributions of the SiC fibers from PCS-20%PVS and PCS. PCS-20%PVS and PCS polymer fibers with the diameter of 11.1 and 19.4 μm shrink about 25% and 40% in diameter, respectively, during pyrolysis process in which they are converted from polymer to ceramics. The average diameters of the SiC fibers are 8.5 and 11.8 μm for PCS-20%PVS and PCS, respectively. The diameter distribution curve for PCS-20%PVS is more sharp than that for PCS. This means that the melt-spinning of PCS-20%PVS polymer is more stable than that of PCS, for the polymer blend changes slowly from melting state to solid state. These fine SiC fibers obtained from the polymer blend are very flexible.

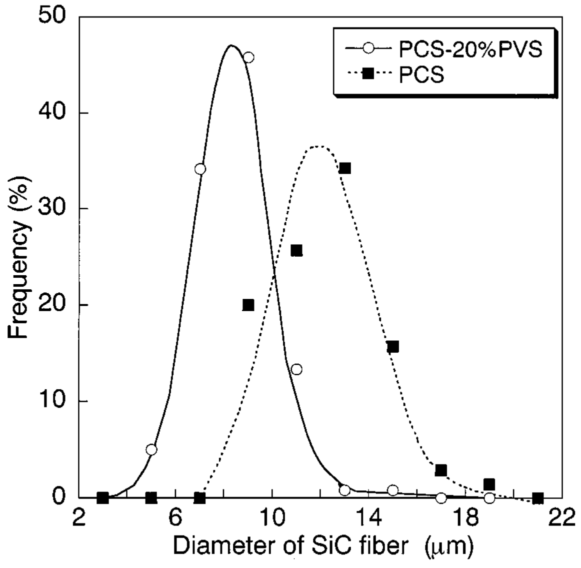


Figure 3 Diameter distributions of SiC fibers obtained from PCS-20%PVS and PCS. Curing dose: 15 MGy; Pyrolysis: 1273 K for 3.6 ks in Ar gas atmosphere.

Fig. 4 shows SEM photographs of the SiC fibers from PCS-20%PVS and PCS. Both the SiC fibers show straight and smooth surfaces, because of sufficient crosslinking of polymers in the fibers. In case of the irradiation dose of 5 MGy, the SiC fiber from PCS-20%PVS coagulated with each other during the pyrolysis process due to insufficient crosslinking [11].

3.2. Properties of SiC fiber

The SiC fibers from PCS-20%PVS and PCS, obtained by the pyrolysis subsequent to the EB curing with the dose of 15 MGy, had the average tensile strengths of 2.5 GPa. The tensile strengths of the SiC fibers were almost the same between the fibers from PCS-20%PVS and PCS, though the average diameters of the fibers are different more than 3 μm.

Fig. 5 shows changes of the tensile strengths of the SiC fibers heat-treated at the temperatures above 1273 K in Ar gas atmosphere. The average diameters of the SiC fibers from PCS-20%PVS and PCS hardly changed by the heat treatments at all temperatures. The average tensile strengths of the SiC fibers from PCS are nearly constant after heat treatment till 1773 K. On the other hand, the average tensile strengths of the SiC fibers from PCS-20%PVS increase with increasing in the heat treatment temperature till 1673 K. The SiC fibers from PCS-20%PVS have higher average tensile strength than those from PCS, e.g., 3.2 GPa from PCS-20%PVS and 2.8 GPa from PCS after the heat treatment at 1673 K. This is due to the smaller diameters of the SiC fibers from PCS-20%PVS than those from PCS (see Fig. 3). The average tensile strength of the SiC fiber from PCS-20%PVS after heat treatment at 1473–1673 K is about 20% higher than that of the SiC fiber pyrolyzed at 1273 K. This suggests that the SiC fibers from PCS-20%PVS need higher pyrolysis temperature than 1273 K. Among the SiC fiber from PCS-20%PVS after heat treatment at 1473 K, there was a fiber that showed the tensile strength of 5.9 GPa. In Fig. 5, the average tensile strength of the SiC fiber from PCS-20%PVS heat-treated at 1773 K reduced abruptly to 1.4 GPa. The reason for this is discussed below (Fig. 8).

Changes of the tensile strengths of the SiC fibers from PCS-20%PVS, cured with γ-ray irradiation in air are also shown in Fig. 5. This SiC fiber (average diameter of 19 μm) was obtained by the curing with the dose of 0.254 MGy in air and pyrolysis at 1373 K for 3.6 ks in Ar gas atmosphere. The SiC fiber contains oxygen atoms in the molecular structure. The tensile strength of the SiC fiber decreases on heat treatment above 1373 K,

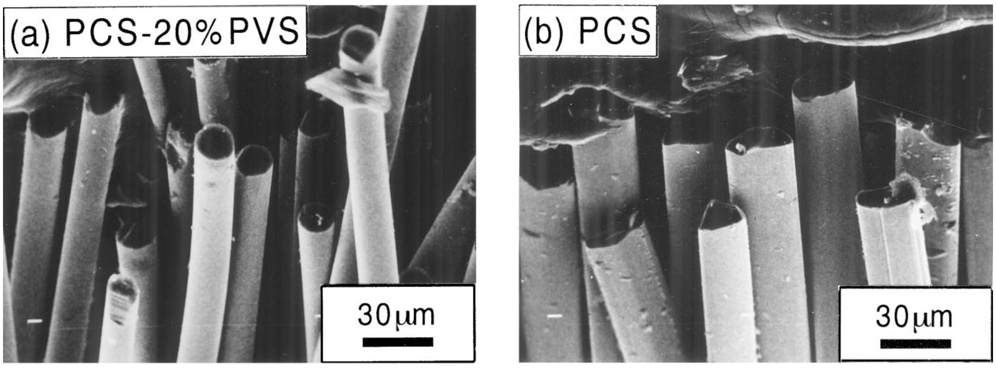


Figure 4 SEM photographs of SiC fibers obtained from PCS-20%PVS and PCS. Curing dose: 15 MGy; Pyrolysis: 1273 K for 3.6 ks in Ar gas atmosphere.

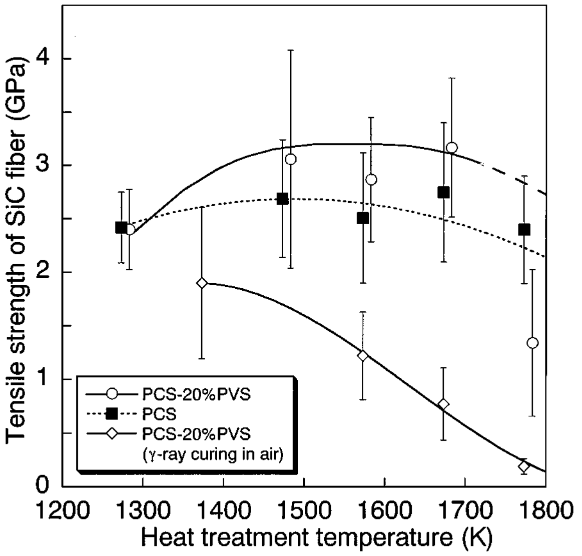


Figure 5 Relationship between heat treatment temperature and tensile strength of SiC fibers. SiC fiber: fibers from PCS-20%PVS and PCS with EB curing under vacuum, and fibers from PCS-20%PVS with γ-ray curing in air; Heat treatment: 1473–1773 K for 3.6 ks in Ar gas atmosphere.

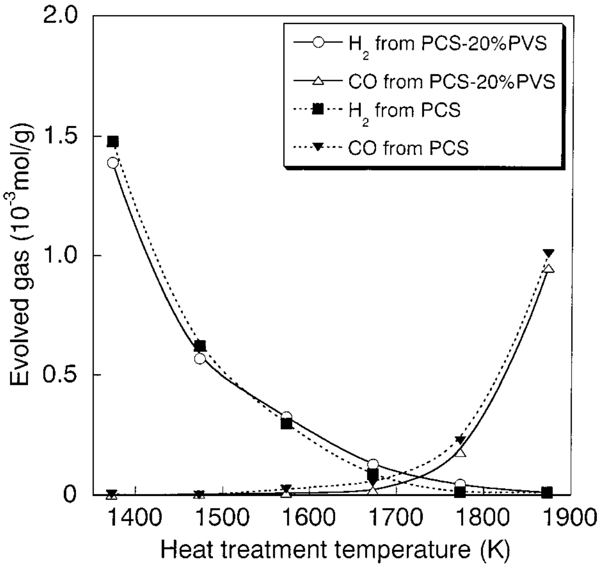


Figure 6 Gas evolution from SiC fibers by heat treatment. SiC fiber: pyrolysis temperature of 1273 K, and curing dose of 15 MGy.

and the fiber loses its tensile strength at the treatment temperature of 1773 K. Thermal resistance of the SiC fibers with EB curing under vacuum is superior to that of fibers cured in air.

Fig. 6 shows the gas evolution from the SiC fibers obtained from PCS-20%PVS and PCS during heat treatment in the temperature ranging from 1373 to 1873 K. Hydrogen (H_2) and carbon monoxide (CO) gases were detected, but our gas chromatography columns cannot detect silicon monoxide (SiO) gas. The H_2 gas evolution in these heat treatments means that inorganization of the polymer fiber does not finish completely in the pyrolysis process at 1273 K. By heat treatment at the higher temperature around 1700 K, inorganization of the fiber is completed, and the tensile strength of the fibers reaches the highest value (see Fig. 5). On the other hand, CO gas starts to evolve on heat treatment at temperatures above 1700 K. This indicates that oxygen atoms are incorporated in the fiber.

The SiC fiber obtained with thermal oxidation curing, which contains more than 15 at% oxygen in the fiber, changes rapidly from amorphous SiC to β-SiC crystal on heat treatment above 1500 K by the following reaction, and loses its tensile strength [12–17].

$$\mathrm{SiC}_{1+X}\mathrm{O}_{Y}\ \text{(amorphous solid)} \rightarrow \beta\text{-SiC (solid)} + \mathrm{SiO}\ \text{(gas)} + \mathrm{CO}\ \text{(gas)} \qquad (1)$$

The tensile strength of the SiC fibers from PCS-20%PVS in Fig. 5 decreased after the heat treatment at 1773 K. This is because the SiC fibers contain a small amount of oxygen atoms as an impurity irrespective of the curing and the pyrolysis of the fibers under inert atmosphere.

Fig. 7 shows typical SEM photographs of the SiC fibers after the heat treatment at the temperature of 1673 and 1773 K in Ar gas atmosphere. In both fibers, after heat treatment at 1673 K, the surfaces of the fibers are smooth, and have no crystal grain (Fig. 7a-1 and b-1). However, at 1773 K, many small crystal grains are shown on the fiber surfaces (Fig. 7a-2 and b-2). As these crystal grains grown by the heat treatment at higher temperature cause fracture in grain boundaries, the tensile strength of the SiC fiber decreases at 1773 K (see Fig. 5).

Fig. 8 shows the depth profiles of carbon, silicon, and oxygen atoms from the surface of the SiC fibers

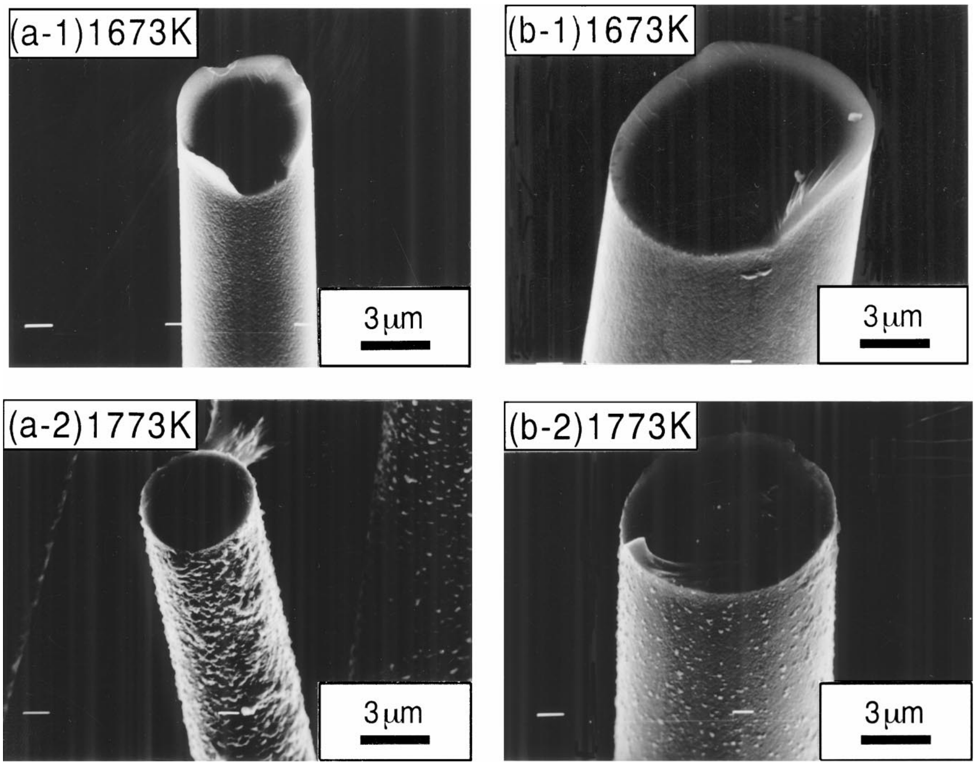
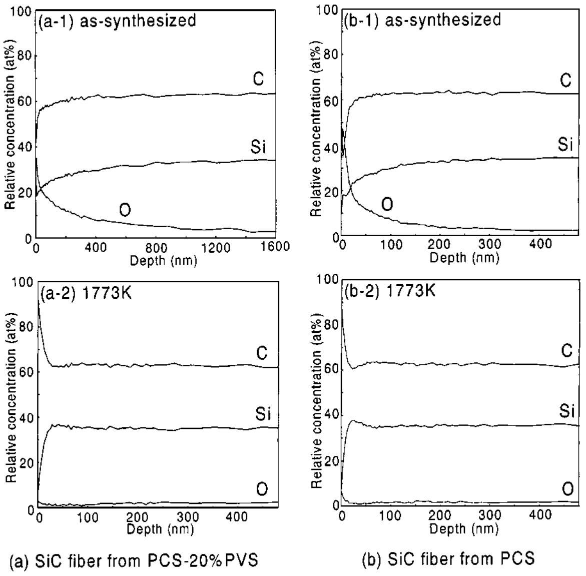


Figure 7 SEM photographs of SiC fibers after heat treatment in Ar gas atmosphere: (a) SiC fiber from PCS-20%PVS heat-treated at 1673 K (a-1) and at 1773 K (a-2) (b) SiC fiber from PCS heat-treated at 1673 K (b-1), and at 1773 K (b-2). SiC fiber: pyrolysis temperature of 1273 K, and curing dose of 15 MGy.



(a) SiC fiber from PCS-20%PVS (b) SiC fiber from PCS

Figure 8 Depth profiles of carbon, silicon, and oxygen atoms in SiC fibers: (a) SiC fiber from PCS-20%PVS as-synthesized (a-1) and heat-treated at 1773 K (a-2), (b) SiC fiber from PCS as-synthesized (b-1) and heat-treated at 1773 K (b-2). SiC fiber: pyrolysis temperature of 1273 K, and curing dose of 15 MGy.

by AES. The vertical axis is relative concentrations of the three kinds of atoms. For the SiC fibers obtained by pyrolysis at 1273 K (Fig. 8a-1 and b-1), the profiles of C atoms and Si atoms are almost similar to each other. In the profile of O atoms, the relative concentration of O atoms in the SiC fiber from PCS-20%PVS is about 35 at% at the surface, about 12 at% at 200 nm in depth, and tails gradually to zero at ∼1600 nm. On the other hand, the relative concentration of O atoms in the SiC fiber from PCS is about 47 at% at the surface, but decreases rapidly with increasing in depth, i.e., oxygen concentration is about 5 at% at 200 nm, that is less than half that in the fiber from PCS-20%PVS. In other words, the fiber from PCS-20%PVS contains more O atoms around the surface than that from PCS. However, the oxygen concentrations of both the SiC fibers are similar to each other at 1600 nm for the fiber from PCS-20%PVS and at 400 nm for the fiber from PCS. This suggests that the main part of O atoms in the fiber is not contained in the original polymers, but in the melt-spinning process, because the curing and the pyrolysis processes were conducted under inert atmosphere. For both SiC fibers heat-treated at 1773 K (Fig. 8a-2 and b-2), oxygen concentration in the fiber is very low, and silicon concentration at the surface of the fiber is also low. This means that the reaction (1) that evolves CO and SiO gases takes place in the SiC fiber, and β-SiC crystal growth on the surface of the fiber. If oxygen content could be lowered in the SiC fiber from PCS-20%PVS, it is possible to improve heat resistance of the fiber above 1773 K.

4. Conclusions

In this paper, a SiC fiber was synthesized from PCS-PVS polymer blend with electron beam curing under vacuum to obtain a fine and high performance SiC fiber.

(1) The SiC fiber from PCS-20%PVS has a smaller average diameter of 8.5 μm than that of 11.8 μm from PCS, and shows a higher average tensile strength of 3.2 GPa than that of 2.8 GPa from PCS after heat treatment at 1673 K. Among the SiC fibers from

PCS-20%PVS after heat treatment at 1473 K, there was a fiber that showed a tensile strength of 5.9 GPa.

(2) Thermal resistance of the SiC fiber obtained from PCS-20%PVS with the electron beam curing under vacuum is superior to that of the SiC fiber obtained with γ-ray curing in air.

(3) The tensile strength of the SiC fiber from PCS-20%PVS decreases after heat treatment at 1773 K due to the crystallization of β-SiC on the fiber surface. Such crystallization is caused by the oxygen atoms incorporated near the fiber surface. Therefore, by controlling the oxygen concentration, a fine SiC fiber with excellent thermal resistance will be synthesized from the PCS-PVS polymer blend.

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Received 13 December 1999
and accepted 26 June 2000