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Synthesis of SiC ceramic fibers from nuclear reactor irradiated polycarbosilane ceramic precursor fibers

Liangping Xiong · Yunshu Xu · Yang Li · Xiulong Xia

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Abstract Polycarbosilane (PCS) ceramic precursor fibers are irradiated in a nuclear reactor and pyrolyzed under inert atmosphere. Bridge structure of Si–CH_2–Si is formed in the irradiated products by the rupture of Si–H bonds and succeeding cross-linking. When irradiated at the neutron fluence of 2.2×10^{17} cm^{-2} under N_2 atmosphere, the gel content and ceramic yield at 1,273 K of PCS fibers are up to 80% and 94.3%, respectively, and their pyrolysis products are still fibrous, which illuminates that the infusibility of PCS fibers has been achieved. FT-IR spectra indicate that the chemical structure of pyrolysis products is very similar to that of pure SiC, while X-ray diffraction curves suggest that β-SiC microcrystals are formed in the fibers, and their mean grain size is about 7.5 nm. The oxygen content (1.69–3.77 wt%) is much lower than that of conventional SiC fibers by oxidation curing method (about 15 wt%). Tensile strength of the SiC fibers is up to 2.72 GPa, which demonstrates that their mechanical properties are excellent. After heat-treated at 1,673 K in air for an hour or at 1,873 K under Ar gas atmosphere for 0.5 h, their external appearance is still undamaged and dense, and their tensile strength decreases to a small extent, which verifies that heat resistance of the SiC fibers is eximious.

Introduction

Recently, silicone carbide (SiC) ceramic fibers have been an attractive candidate for reinforce material in advanced composites, which are applied in the fields of aerospace, aviation, nuclear energy, etc. This is attributed to the excellent performances of SiC fibers, for example, high tensile strength and stiffness, outstanding oxidation resistance at elevated temperature, and good miscibility with ceramics, metals, and resins [1–4].

SiC ceramic fibers have been mainly fabricated by pyrolysis of organosilicon polymer fibers called ceramic precursor fibers such as polycarbosilane (PCS). In this process, the precursor polymers are synthesized, melt-spinned to finer fibers, cured, and then pyrolyzed to ceramic fibers [3–6]. Because PCS fibers tend to melt when heated to 500 K, leading to unshaped pyrolysis products, it is necessary to cure the polymer fibers before pyrolysis to make them infusible, then to increase the ceramic yield and obtain fibrous pyrolysis products.

Thermal oxidation curing is a conventional and convenient method. However, a large amount of oxygen atoms (about 15 wt%) is introduced in the fibers, resulting in the release of carbon monoxide gas and the deterioration of the fibers' tensile strength at temperature above 1,473 K [6, 7]. An oxygen-free curing process of PCS fibers has been developed by exposure to electron beam or γ-rays. SiC ceramic fibers obtained from pyrolysis of PCS fibers cured in this way exhibit excellent thermal stability up to 2,000 K [8–10], as a result of extremely low oxygen content in the fibers. However, the required dose for infusible PCS is about 10 MGy–15 MGy [3, 5, 11, 12], which makes it hard on irradiation equipments, low in efficiency, and high costs of production.

On the other hand, the radiation field of a nuclear reactor is so intense that it is seldom used in the research work of polymeric materials. Moreover, neutrons from a reactor incline to transfer their energy to hydrogen atoms because of the fine distinction between the weight of the two kinds

L. Xiong (✉) · Y. Xu · Y. Li · X. Xia
Institute of Nuclear Physics and Chemistry, China Academy of Engineering Physics, Mianyang 621900, China
e-mail: pinger1981@ustc.edu

of particles, which is favorable to the cleavage of C–H and Si–H bonds in PCS and succeeding cross-linking and formation of SiC framework. Therefore, the curing of PCS fibers can be achieved by irradiation in a nuclear reactor in theory. In the present study, PCS fibers are irradiated in a nuclear reactor under inert atmosphere, and then pyrolyzed to synthesize SiC ceramic fibers. The chemical structure and thermal behaviors of the cured PCS precursor fibers and the properties of their pyrolyzed products are analyzed and characterized.

Experimental procedure

Curing and pyrolysis of PCS fibers

Curing of PCS ceramic precursor fibers

PCS fibers were wrapped with a piece of aluminum foil, placed into a quartz tube, which was vacuumized, filled with high-purity nitrogen (99.99%), and then sealed. The fibers in the tube were irradiated in a nuclear reactor at a series of thermal neutron fluences. The neutron fluence rate was 10^{13} cm^{-2} s^{-1}. During the irradiation, the tubes were cooled with water to prevent any temperature increment. After irradiation, the tubes were set away until the radioactivity came near to the background, and then heat-treated at 423 K for 0.5 h to quench active species produced by the irradiation in the fibers, which were prevented from reacting with oxygen in air in this way.

Pyrolysis of cured PCS ceramic precursor fibers

The cured PCS fibers were placed into a quartz tube, and then pyrolyzed in an electrical resistance tubular furnace to convert into SiC ceramic fibers. The furnace was vacuumed with a pump, and then filled with high-purity argon, which was repeated for three times to eliminate air in the furnace. Then the fibers were heated from the ambient temperature up to 1,273 K, with the heating rate of 200 K h^{-1}, and held at this temperature for 2 h, then cooled to room temperature, with argon flowing continuously. The products were black fibers with metal gloss.

Measurement and analysis

Structure and thermal decomposition behaviors of cured PCS fibers

The gel content in the irradiated PCS fibers was measured by extraction at 423 K for 48 h, with xylene as eluent. The samples were dried and weighed, then the gel content was calculated with the following formula: $\text{Gel}\% = \frac{w_2}{w_1} \times 100\%$, wherein, W_1 and W_2 are the weight of the sample before and after extraction, respectively.

The Fourier transform infrared (FT-IR) spectra were recorded in the 400–4,000 cm^{-1} range, from pressed pellets made from a finely ground mixture of KBr crystal grain and the samples (weight ratio: about 1%).

Thermal decomposition behaviors and ceramic yields of the precursor fibers were investigated by thermal gravimetric analysis (TGA). Samples were heated from the ambient temperature up to 1,273 K in flowing argon (20 cm^3 min^{-1}), with a heating rate of 10 K min^{-1}. Approximately 10 mg of each sample was placed in an open alumina pan with an empty pan as the reference.

Structure and properties of SiC ceramic fibers

The FT-IR spectra of product fibers were recorded in the same way as PCS precursor fibers.

The microscopic external morphology of the obtained SiC fibers were observed by scanning electron microscopy (SEM: Stereoscan S440, Leica Cambridge LTD). Samples studied using the SEM were coated with gold.

The X-ray diffraction (XRD) spectra were carried out on the D/Max-rA diffractometer with Cu-Kα. The apparent mean grain size (L) of the β-SiC crystalline phase present in the samples was calculated from the width (D) of the (111) diffraction peak at mid-height, according to the following Scherrer equation: $L = K\lambda/D \cos\theta$, wherein K is a constant (taken as 1), λ is the Cu-Kα wavelength (i.e. $\lambda = 0.154$ nm), and θ is the Bragg angle ($\theta = 17.8°$ for β-SiC (111)).

The oxygen content of SiC fibers was measured with an IRO-I oxygen determinator under argon atmosphere. Samples were wrapped with nickel foils as flux metals.

The tensile strength of SiC fibers was measured at ambient temperature using a monofilament tensile testing machine (LLY-06B, Laizhou Electronic Machine Ltd., Shandong, China) with a gauge length of 20 mm and a crosshead speed of 10 mm min^{-1}. Maximum tension load $P_{\max}$ was measured, then the tensile strength (σ) of a monofilament was calculated from the following equation: $\sigma = \frac{4P_{\max}}{\pi D^2} \times 10^3(\text{GPa})$, wherein, D is the diameter of the monofilament, and π is the circumference rate constant. The average tensile strength was obtained from 20 specimens.

The SiC fibers were placed into an alumina crucible and then heat-treated in a Carbolite BLF18/3 chamber furnace (Barloword Scientific Co., UK) with two ways: holding at 1,673 K for 1 h in air and at 1,873 K for 0.5 h under Ar gas atmosphere, respectively. After heat-treated, tensile strength of SiC fibers was tested, and microscopic external morphology of the SiC fibers were observed by SEM.

Results and discussion

Chemical structure and thermal behaviors of nuclear-reactor-irradiated PCS precursor fibers

Figure 1 shows the FT-IR spectra of PCS precursor fibers before and after irradiation. When the neutron fluence increases, the intensity of absorption band at 2,100 cm^{-1} assigned to ν(Si–H) decreases apparently, which indicates that irradiating PCS fibers in a reactor causes the rupture of Si–H bonds. The reason is that the mass of a neutron and a H atom is almost the same; when there is elastic collision between a neutron with high energy and a still H atom, it is likely that the energy is delivered to H atom mostly or even entirely. Moreover, the Si–H bond energy is quite low (about 315 kJ/mol) [13]; therefore, Si–H bonds in PCS fibers tend to rupture when exposed in a nuclear reactor. Free radicals are produced with the rupture of Si–H bonds, then join and cross-link to form bridge structure of Si–CH_2–Si, which has been testified by the increased absorption band ν(Si–C) in Si–CH_2–Si at 734 cm^{-1}, compared with the relatively stable absorption band δ_s(Si–CH_3) at 1,251 cm^{-1}. This structure would make up the SiC ceramic fibers' framework when pyrolyzed.

Figure 2 shows the relationship between gel content of the PCS precursor fibers and the irradiation neutron fluence. It is apparent that gel content increases with irradiation neutron fluence, and it is up to 95% at the neutron fluence of 3.5×10^{17} cm^{-2}, exceeding the maximum gel content of PCS fibers cured by EB and γ-ray irradiation, which is about 86–90% in previous studies [12].

When the fibers were irradiated, some soluble components such as PCS of low molecular weight (LPCS) were connected to form insoluble components of higher molecular weight, so the gel content increased. Former researchers [14] have indicated that when gel content of PCS fibers is above 75%, their pyrolysis products are fibrous. In this study, gel content is 80% when PCS fibers are irradiated at the fluence of 2.2×10^{17} cm^{-2}, which meet the demand of curing.

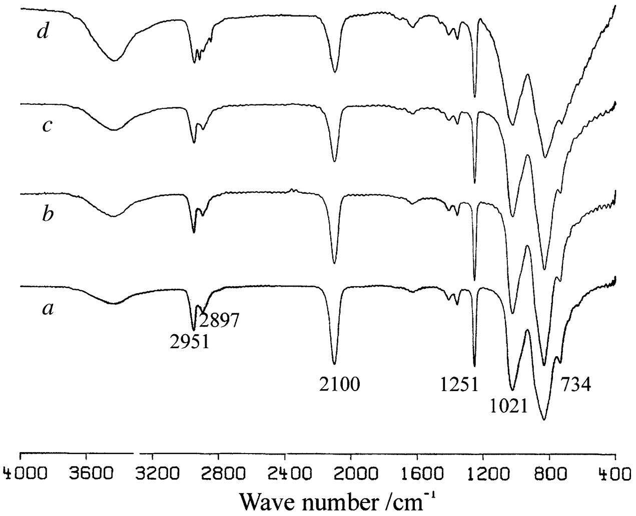


Fig. 1 FT-IR spectra of PCS precursor fibers irradiated to various neutron fluences (**a**) controlled; (**b**) 8.7×10^{16} cm^{-2}; (**c**) 2.6×10^{17} cm^{-2}; (**d**) 4.3×10^{17} cm^{-2}

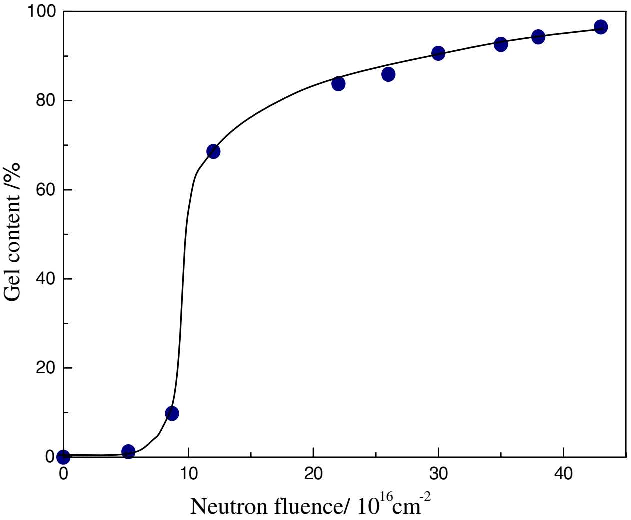


Fig. 2 The effect of neutron fluence on the gel content of PCS precursor fibers

Pyrolysis behavior of nuclear-reactor-irradiated PCS precursor fibers

The thermo gravimetric traces of PCS fibers are shown in Fig. 3. It is noteworthy that the residual mass ratio at 1,273 K is about 95% for the irradiated PCS fibers, while it

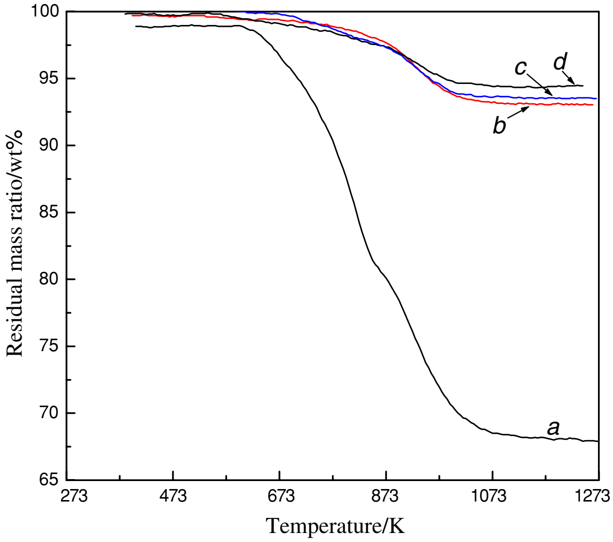


Fig. 3 TGA curves of PCS precursor fibers irradiated at various neutron fluences (**a**) controlled; (**b**) 5.2×10^{16} cm^{-2}; (**c**) 8.7×10^{16} cm^{-2}; (**d**) 2.6×10^{17} cm^{-2}

is only about 68% in the case of the un-irradiated fibers. Compared with EB and γ-ray irradiation, for which the maximum ceramic yield is about 81–86%, irradiation in a nuclear reactor can obtain higher ceramic yield. The PCS fibers' pyrolysis process takes place in three consecutive stages. In the first stage (up to 603 K), a very low rate of weight loss of less than 2% occurs and this is characteristic of high molecular weight polymers. In the second stage (603–833 K), the weight loss ratio is about 18.5%, due to the volatilization of polycarbosilane of low molecular weight (LPCS). In the third and final stage (above 833 K), carbon silicides of low molecular weight and methane were released, and it loses 12% of its weight. However, after irradiation, the temperature at which PCS fibers begin to lose weight rises to 733 K, and the loss weight is merely about 5%. When PCS fibers are irradiated, bridge structure between the molecules is formed. Most of LPCS molecules have been connected to form network polymers of high molecule weight, so they are not volatilized when heated. Thatis why the ceramic yield increase is so considerable. This is just what we expect.

Comparing with the gel content results (Fig. 2), we can infer that when irradiated at lower neutron influence, some of the LPCS are connected to form molecules of higher weight; those are not volatilized when heated but still can be solute in xylene, which caused the high ceramic yield but is not so for gel content. As the neutron influence increased, these molecules are cross-linked and cannot be volatilized or solute.

The pyrolysis products of PCS fibers irradiated at several neutron fluences take on different appearance. The pyrolysis products of un-irradiated PCS fibers are lumpy and apt to disintegration. Pyrolysis products of the PCS fibers irradiated at lower neutron fluences ($\leq 5.2 \times 10^{16}$ cm^{-2}) are massive, while those of the PCS fibers irradiated at higher neutron fluences ($\geq 2.2 \times 10^{17}$ cm^{-2}) are fibrous, and SEM photos (Fig. 4) show that the surface of the fibers is very smooth and compact. This is because uncured PCS fibers are fragile and tend to melt when heated, at the same time a large amount of gases are released, leading to the lumpy products. For PCS fibers irradiated at lower neutron fluence, the degree of cross-linking is quite low, so they melt when heated, but there is only a small amount of gas released, leading to massive products. For the PCS fibers irradiated at higher neutron fluence, the degree of cross-linking is quite high, so the fibers do not melt when heated and release little amount of gas and, as expected, fibrous products are obtained.

Structure of SiC ceramic fibers

Chemical structure and crystal structure of the obtained fibers are shown in Figs. 5 and 6, respectively. The absorption peaks in the FT-IR spectra of the obtained fiber

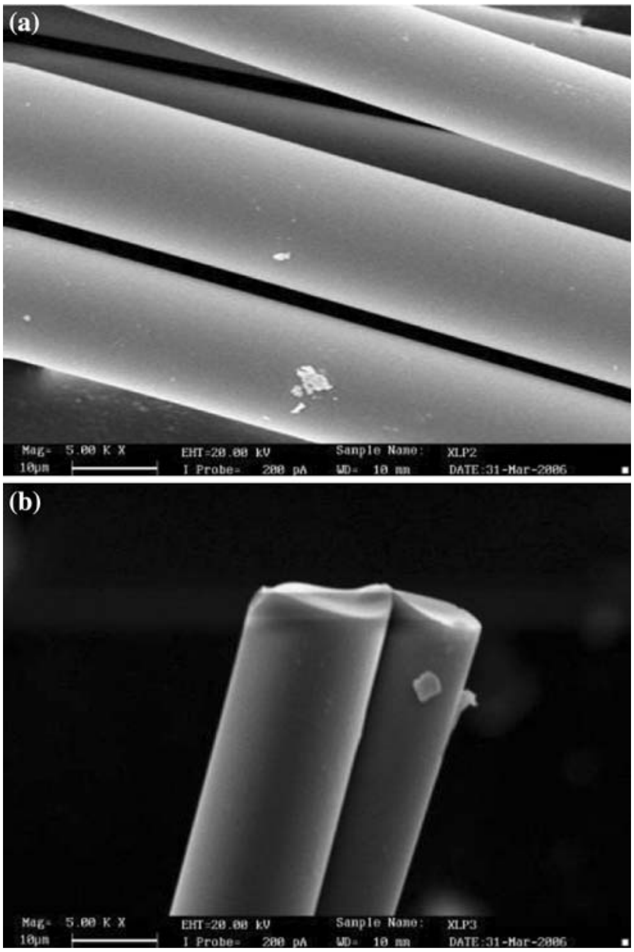


Fig. 4 SEM photos of the pyrolysis products of PCS precursor fibers irradiated by a nuclear reactor (Neutron fluence: (**a**) 2.6 × 10^{17} cm^{-2}; (**b**) 4.3 × 10^{17} cm^{-2})

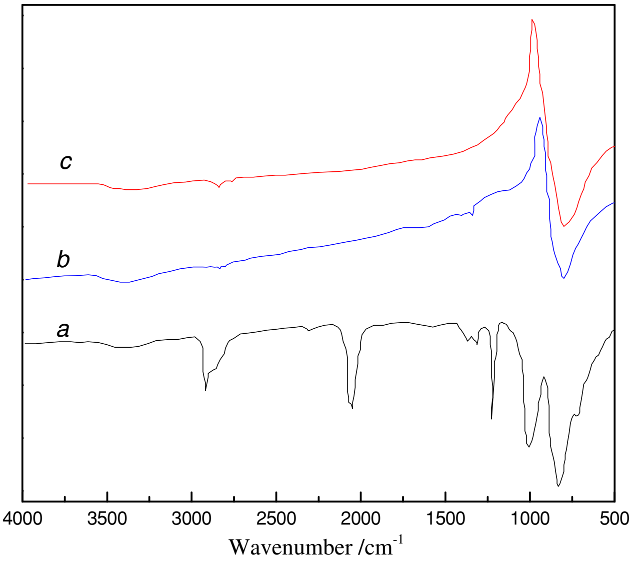


Fig. 5 FT-IR spectra of cured PCS precursor fibers' pyrolysis products (**a**) cured PCS precursor fibers; (**b**) pyrolysis products; (**c**) pure SiC

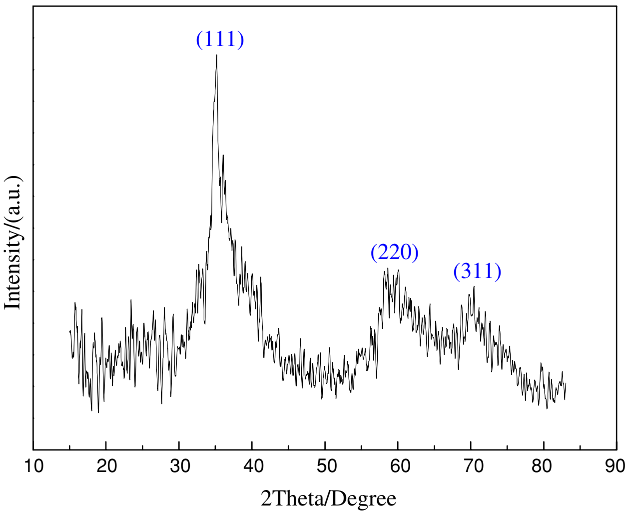


Fig. 6 XRD curve of SiC ceramic fibers

are very similar to those of pure SiC. In the XRD curve, three main peaks, assigned to the (111), (220), and (311) reflections of β-SiC are observed (corresponding to a d spacing of 0.251, 0.154, and 0.134 nm, respectively). Calculated from the Scherrer equation, the mean grain size of β-SiC microcrystals is about 7.5 nm at room temperature. This is far less than 40 nm of Nicalon fiber, but a little more than 5 nm of Hi-Nicalon fiber [9].

Tensile strength of SiC ceramic fibers

Tensile strength of SiC monofilament is calculated from the following equation: $\sigma = \frac{4P_{\max}}{\pi D^2} \times 10^3(\mathrm{GPa})$, wherein $P_{\max}$ is measured and evaluated from the SEM photos, and the diameter D is 12 µm. The relationship between neutron fluence of PCS precursor fibers and obtained SiC fibers' tensile strength is shown in Fig. 7, which obeys approximately a linear law. SiC fibers tensile strength increases with the elevation of neutron fluence, and it is up to 2.72 GPa, which is equivalent to the tensile strength of Nicalon fiber (2.6–3.0 GPa).

Oxygen content of SiC ceramic fibers

The oxygen content of SiC ceramic fibers is shown in Table 1. The lowest oxygen content is 1.69 wt%, and the highest one is 3.77 wt%. They are quite low when compared with thermal oxidation cured SiC fibers, oxygen content of which is about 15 wt%; however, compared with about 0.5 wt% oxygen content of Hi-Nicalon, prepared from EB irradiation cured PCS fibers by Nippon Carbon Co., they are a little high. That may be because in the course of preparation, air introduction could not be avoided owing to the incomplete experimental facility, which should be improved in subsequent experiments.

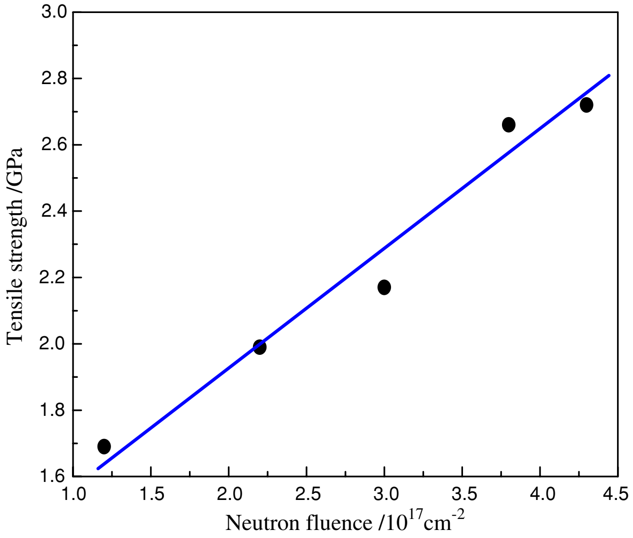


Fig. 7 The relationship between neutron fluence and SiC fibers' tensile strength

Table 1 Oxygen content of SiC fibers

Curing neutron fluence (10^{17} cm^{-2})	1.2	2.2	3.0	3.8	4.3
Oxygen content of SiC fibers (wt%)	2.52	3.16	1.69	1.99	3.77

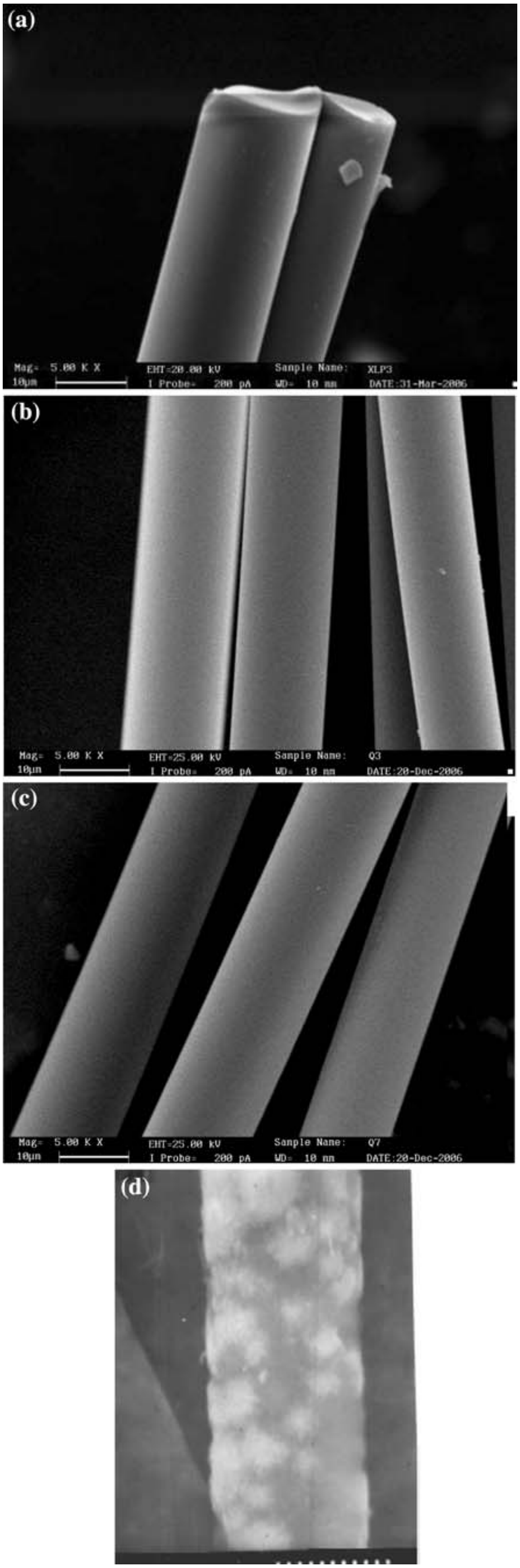
Heat resistance of SiC ceramic fibers

The data of tensile strength of SiC ceramic fibers after heat-treatment are listed in Table 2. It has decreased to a small extent when the fibers are heat-treated at 1,873 K under Ar gas atmosphere for 0.5 h, which illuminates that the SiC fibers' heat resistance is prominent.

SEM photos of the SiC ceramic fibers after heat-treatment are shown in Fig. 8. These photos indicate that the structures of the fibers are quite intact, and there is no visible fissure at the heat-treated fibers' surface (Fig. 8b, c). Compared with the SiC fibers obtained from thermal oxidized PCS fibers, such as Nicalon$^{\mathrm{TM}}$ fibers, which become loose when heat-treated at 1,873 K for 0.5 h (Fig. 8d), the SiC fibers obtained from irradiation cured PCS fibers

Table 2 Tensile strength of SiC fibers before and after heat-treatment

Curing neutron fluence (10^{17} cm^{-2})	Tensile strength (GPa)	
	Before heat-treatment	After heat-treatment (1,873 K, under Ar gas atmosphere, 0.5 h)
4.3	2.72	2.58
3.8	2.66	2.55
3.0	2.17	2.08



◀ **Fig. 8** SEM photos of SiC fibers before and after heat-treating (**a**) SiC fibers before heat-treating; (**b**) under Ar gas atmosphere, 1,873 K, 0.5 h; (**c**) in air, 1,673 K, 1 h; (**d**) oxygen cured, under He gas atmosphere, 1,873 K, 0.5 h [15]

exhibit more excellent thermal stability. Because a large number of oxygen (about 15 wt%) is introduced in Nicalon^{TM} fibers, oxidation reaction occurs above 1,473 K, resulting in the evolution of volatile products (assumed to be CO and SiO) and the generation of air bubbles [8, 9, 14, 15], which causes the destruction of the fiber structure and the deterioration of their mechanical properties, while for the fibers resulting from the pyrolysis of nuclear-reactor-irradiated PCS precursor fibers, with low oxygen content, oxidation reaction does not take place at high temperature, so they exhibit prominent heat resistance, which could afford application into hot environment.

Conclusion

The infusibility of PCS ceramic precursor fibers has been achieved by irradiation in a nuclear reactor for the first time. When the fibers are irradiated at the neutron fluence of 2.2×10^{17} cm^{-2} under N_2 atmosphere, the gel content and ceramic yield go up to 80% and 94.3%, respectively. Their pyrolysis products are fibrous, which meets the demand of curing. In course of irradiating, a part of Si–H bonds are broken, and bridge structure of Si–CH_2–Si is formed, making the irradiation products infusible and insoluble.

As expected, SiC ceramic fibers with low oxygen content have been obtained from pyrolysis of the nuclear-reactor-irradiated PCS precursor fibers. These SiC fibers exhibit excellent heat resistance and tensile strength, and β-SiC microcrystals with the mean grain size of 7.5 nm are formed in the fibers.

In conclusion, irradiation by a nuclear reactor can make the PCS ceramic precursor fibers infusible and insoluble, and excelled exposure to electron beam or γ-rays in the aspects of gel content and ceramic yield of the irradiated products. Moreover, SiC ceramic fibers with outstanding performances, such as heat resistance and mechanical properties, can be prepared from nuclear-reactor-irradiated PCS precursor fibers.

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