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LETTER

Irradiation pre-curing plus oxidation curing for rapid preparation of silicon carbide fibers

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Small diameter high-performance silicon carbide (SiC) fibers are commercially produced by polymer precursor route developed by Yajima and his co-workers [1–5]. The processing includes synthesizing polycarbosilane (PCS) precursor, melt-spinning to obtain as-spun fibers, curing by oxidation [6, 7] or electron beam irradiation [8, 9] to render the fibers infusible in the subsequent pyrolysis, and finally pyrolyzing to produce SiC fibers.

Melt-spinning and curing present the biggest challenges in silicon carbide fiber processing. PCS is extremely weak and brittle so that fiber breakage occurs frequently during melt-spinning, making continuous spinning very difficult [10]. During oxidation or irradiation curing, a large amount of heat is generated [2, 11], so that the fibers may partially fuse and stick together. To avoid this, extremely low heating rate or irradiation dose rate is used, making the curing very lengthy, up to 15 h. Irradiation curing is significantly more costly than oxidation curing, but it can produce silicon carbide fibers with much lower oxygen content and hence better thermal stability [8, 9]. Therefore, which curing method to select depends largely upon the maximum service temperature and the production cost of the final ceramic fibers.

Generally speaking, PCS with lower average molecular weight is less brittle and easier to spin. However, such precursor fibers have relatively low melting point and hence are more likely to fuse during curing. The PCS with higher molecular weight has a less tendency to melt during curing, but is more brittle and hence more difficult to spin. Therefore, the suitable PCS is actually a compromise between spinning and curing.

In this work, PCS with low melting point and excellent spinning ability is used as the precursor. The precursor fibers are first irradiation pre-cured at low dosage to raise its melting point, and then quickly oxidation-cured to render them infusible. The purpose is to reduce the stringent requirements for PCS, minimizing the difficulties in both melt-spinning and curing without significantly increasing the processing cost. To our best knowledge, no similar research has been documented so far.

The PCS precursor was synthesized according to the method developed by Yajima and his colleagues [3, 4, 12]. Its average molecular weight (M_n) is 1210 and its melting point is 196 °C. The precursor was put into the reservoir of a laboratory piston-type melt-spinning machine (MMCH05, Chemat, USA), and then heated to the melt-spinning temperature under the protection of high purity N_2 to prevent it from oxidation. The polymer melt was extruded through a single-hole spinneret and collected on the winding bobbin. The as-spun fibers were irradiation pre-cured in flowing Helium with a 2 MeV electron accelerator (GJ2, Xianfeng Co. Ltd., China). The dose rate was 0.42 KGy s^{-1} until the set dosage was reached. For oxidation curing, the pre-cured fibers or the as-spun fibers were placed into a tube furnace and then heated in hot air. The residence time at the set temperature was 30 min, and the flow rate of air was

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200 cm^3/min. For pyrolysis, the oxidation-cured fibers were placed into a perforated graphite boat. They were heated to 1250 °C in high-purity N_2 at a heating rate of 5 °C min^{-1}, and then furnace-cooled without any residence at the set temperature.

Melting point was measured using a melting point apparatus (WRS-2A, Shanghai Precision & Scientific Instrument Co. LTD., China). Ten measurements were made for each sample and the average was taken as the melting point. Soxhlet extraction method was used to measure the gel fraction of the fibers after curing. The extraction solvent was xylene, and the extraction time was 24 h. Oxygen content was determined using Oxygen Nitrogen Analyzer (EMGA-620W, Horiba, Japan). At least three measurements were made for each point and the average value was used. The tensile strength of single SiC fibers was measured using a universal tensile testing machine (SUN2500, Galdabini, Italy). The gauge length was 25 mm and the crosshead speed was 1 mm min^{-1}. Twenty-five fibers were tested and the average was used. Scanning electron microscopy (XL30, Philips-FEI, Eindhoven, Netherlands) was used for fiber diameter determination.

The major purpose of the irradiation pre-curing is to raise the melting point of the precursor fibers, preventing them from fusion during the followed oxidation curing. Figure 1 shows the melting point as a function of irradiation dosage. The melting point increases progressively with dosage, rising from 196 to 292 °C after 2 MGy. According to Okamura [9], three kinds of free radicals, $-\dot{Si}(CH_3)-CH_2-$, $-H\dot{Si}-CH_2-$ and $-HSi(CH_3)-\dot{C}H-$ are generated during irradiation in a non-oxidative atmosphere. They recombine to form Si–C bonds, resulting in cross-linking.

Some un-reacted free radicals remain fairly stable in oxygen-free atmosphere at room temperature after irradiation. When exposed to air, however, they are oxidized instantly, resulting in the increase of oxygen content in the fibers [9]. Therefore, for the preparation of low oxygen silicon carbide fibers, annealing at about 500 °C in inert gas is required after irradiation to have the free radicals annihilated. In this work, no annealing is carried out, so that the oxygen content after curing at 1.5 MGy is 2.05%, much higher than that of the as-spun PCS fibers, 0.60%.

The as-spun fibers (designated as PCS) and the pre-cured fibers at 1.5 MGy (designated as PCS-1.5) were heated in air to 160 °C at a heating rate of 10, 60, 180 or 300 °C h^{-1}, respectively, and then maintained for 30 min. For the PCS-1.5, no fusion occurred during oxidation curing for all heating rates. But for the PCS, only the fibers cured at the slowest heating rate (10 °C h^{-1}) survived, and all the rest fused. This clearly shows that the pre-cured precursor fibers can be easily oxidation-cured at fast heating rate without fusion, reducing the curing time by over 10 h. Therefore, the PCS with low melting point and excellent spinning ability can be used as the fiber precursors, solving the contradictory requirements for the precursors by melt-spinning and curing.

Figure 2 shows the oxygen content and gel fraction as a function of oxidation temperature. For the given oxidation temperature or the given oxygen content after oxidation curing, the gel fraction of PCS-1.5 is higher than that of PCS. Gel fraction is a measure of the degree of cross-linking. The higher it is, the less of the tendency for the fibers to fuse during the subsequent pyrolysis it has. In other words, PCS-1.5 is better cured than PCS. This can be explained as follows. During oxidation curing, the Si–H groups are initially oxidized to form Si–OH groups. This eaction has no contribution to cross-linking, and is called "ineffective oxidation". As the concentration of Si–OH groups grows, they react by condensation polymerization,

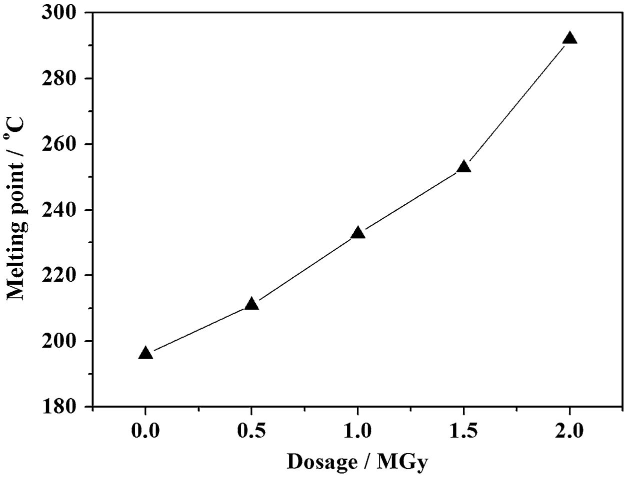

Fig. 1 Melting point of fibers as a function of irradiation dosage

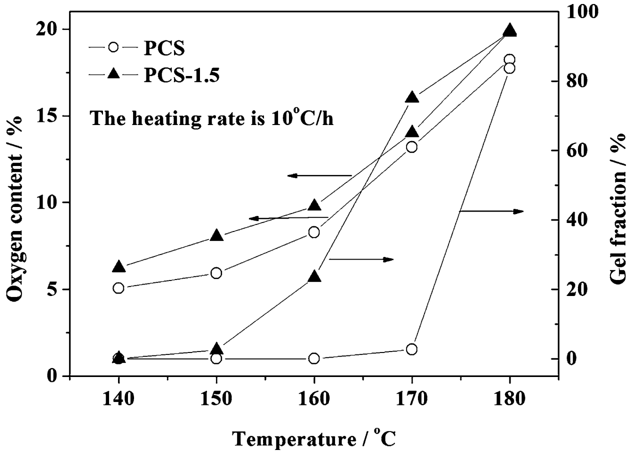

Fig. 2 Oxygen content and gel fraction as a function of oxidation temperature

Table 1 Properties of the ceramic fibers[a]

Oxidation temperature (°C)	PCS		PCS-1.5	
	Oxygen content (%)	Tensile strength (GPa)	Oxygen content (%)	Tensile strength (GPa)
140	6.07	L	8.58	L
150	7.05	L	10.03	1.87 ± 0.57
160	9.73	L	12.42	3.46 ± 0.74
170	14.52	2.87 ± 0.70	15.65	3.48 ± 0.73
180	19.36	2.00 ± 0.77	19.45	2.40 ± 0.64

L lost shape during pyrolysis because of inadequate curing

[a] The heating rate for oxidation curing is 10 °C h^{-1}

releasing water and forming Si–O–Si linkage [6, 13, 14]. The Si–O–Si linkage bridges PCS chains, making them cross-linked. At low irradiation dosage, Si–H is the major bonds broken to form Si-free radical [9]. That is, the irradiation reduces the Si–H concentration and hence the ineffective oxidation.

The properties of ceramic fibers are shown in Table 1. For the PCS fibers, the oxidation curing temperature must be 170 °C or above to avoid losing fiber shape in pyrolysis, while for the PCS-1.5 fibers, only 150 °C is needed to make the fibers infusible. This is consistent with the higher gel fraction for the PCS-1.5 fibers after oxidation curing or its higher degree of cross-linking.

The results also show that the tensile strength of the ceramic fibers is a function of the degree of oxidation. Either under-curing or over-curing will lead to lower fiber property as reported elsewhere [15]. With insufficient curing, the fibers may stick together at some isolated points during pyrolysis, increasing the number density of surface defects and reducing the fiber strength. With excessive curing, the cured fibers become less flexible and rich in oxygen at surface, making them more prone to surface damage during the subsequent handling and pyrolysis. The maximum tensile strength from the pre-cured fibers is higher than that from the directly oxidation-cured fibers. The plausible explanation is that the irradiation pre-curing plus oxidation curing gives the cured fibers with a higher degree of cross-linking and lower density of internal flaws in comparison with the directly oxidation-cured fibers.

The effect of heating rate during oxidation curing on the tensile strength of the final ceramic fibers from PCS-1.5 is shown in Fig. 3. The tensile strength decreases gradually with heating rate. Oxidation curing involves diffusion-controlled reactions. When the heating rate is too high, the fiber surface will be over-cured and the interior under-cured. They all tend to create defects during pyrolysis, reducing tensile strength [15]. Therefore, a compromise between high tensile strength and high productivity should be made in the preparation of silicon carbide fibers.

In summary, polycarbosilane (PCS) with low melting point and good spinning ability is used as the precursor of silicon carbide fibers in order to reduce the difficulty in melt-spinning. When these precursor fibers are pre-cured by electron beam irradiation at low dosage, their melting point can be raised, so that the fibers can then be quickly cured by oxidation without fusion, reducing the total curing time by over 10 h. The pre-curing makes the subsequent oxidation more efficient because of the reduction of Si–H bonds and the formation of Si–C cross-linkage. The tensile strength of the ceramic fibers prepared from the pre-cured fibers is also higher than that from the directly oxidation-cured fibers.

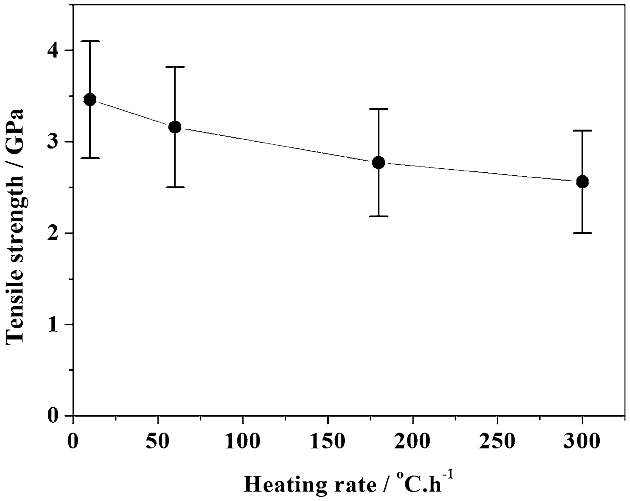

Fig. 3 Effect of heating rate during oxidation on tensile strength of the ceramic fibers from PCS-1.5

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