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Effect of oxygen content on tensile strength of polymer-derived SiC fibers①

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[Abstract] Air-curing is usually applied to the polymer-derived SiC fibers and, as a result, oxygen is embedded to the material. An effective relationship between oxygen content of the SiC fibers and mass gain of their precursor fibers was established. Results also showed that oxygen content has a great influence on the mechanical properties and excellent tensile strength is usually obtained at the oxygen content of 12% ~ 13%, similar to the density of SiC fibers. Oxygen content has a positive effect on the ceramic yield, and thus, is good to the density and tensile strength; while, oxygen content is also negative to volume content of SiC phase and crystallization of the SiC fibers, and thus, detrimental to the density and tensile strength. Both of the two effects result in the peak behavior of the tensile strength of SiC fibers.

[Key words] SiC fiber; oxygen content; mechanical property; polymer-derived ceramic
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1 INTRODUCTION

The development of the Nicalon fibers, obtained by pyrolysis from organic or organometallic polymeric precursors, is attracting considerable interest as it offers the possibility of developing a new generation of composites for high temperature[1~5]. The precursor route has some important advantages with respect to more conventional techniques[6~9]: 1) it requires lower temperature, 2) polymeric precursors can be obtained under different states before firing (e.g. as bulk bodies, green films or fibers), 3) polymeric precursors are available with a variety of compositions as single species or as mixtures, a feature allowing the design of ceramics with specific properties.

Since the first generation SiC fibers prepared by Yajima et al in 1975[10], the precursor route has been characterized as a four-step process, namely, synthesis, spinning, curing and pyrolysis[4]. In the process, curing is a very essential step because the fiber would lose most mass and could hardly retain its cylindrical shape during the subsequent pyrolysis if curing, a process to render the green fiber crosslinked and infusibilized, is absent[11,12].

Cylindrical SiC fibers may not be obtained from uncured or poorly cured precursor fibers, not to mention their mechanical properties. Therefore, it is necessary to make a thorough understanding of the curing so as to obtain excellent SiC fibers. The most common and easy curing process, being used in Nicalon fibers, is air curing during which oxygen reacts with the Si-H bonds and creates Si-O-Si bridge bonds. As a result, oxygen is embedded to the ultimate SiC fibers[13]. By weighting the oxygen content and relate them with mechanical properties of the fiber, we have received some useful information.

2 EXPERIMENTAL

The polycarbosilane (PCS) polymer was synthesized from polydimethylsilane at normal pressure in our laboratory. Its average molecular number was about 1 600 and the melting point was 213 ±3 ℃. The PCS was melted at about 300 ℃ in N_2 and spun into fibers under pressure. The PCS fibers were 20 ± 2 μm in diameter.

The green fibers were then air cured up to 195 ℃ at a certain heating speed from the room temperature to 170~ 195 ℃ and the retaining time was varied to obtain different curing degrees (namely, to obtain different oxygen contents).

Afterwards, the cured PCS fibers (0.5 g) were put into a silica tube, and the tube was evacuated and filled with high purity nitrogen. The tube was heated in an electric furnace to 1 250 ℃ with a heating rate of 2 ℃/min and held at the temperature for 30 min. Then, it was cooled in the tube to room temperature. During the whole process (24 h or so), a high purity nitrogen flow was controlled at a constant rate of 1 mL/min.

3 CHARACTERIZATION

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To characterize curing degree of the fibers, three indexes were applied. One is mass gain, which is a result of the oxidation of PCS and was recorded as the mass increase percentage during curing. The other is the reaction degree of Si-H bond whose data could be calculated from IR spectra. And gel content, the three, is a usual index to characterize the solubility of macromolecules[14,15]. Here, a solvent of benzene and a 48 h reflux time were applied to get the gel content results.

Oxygen content of the PCS or SiC fibers was determined with a nitrogen/oxygen analyser (TC-436, LECO, USA). The sink-float method was used to measure pyrolyzed fiber's density, following a simplified ASTM C729-75 stardard test. Solutions were prepared by mixing α-bromonaphthalene and sym-tetrabromoethane in the range of 2.30 to 2.80 g/cm^3 with increments of 0.05 g/cm^3.

The morphology of the SiC fibers was observed by scanning electron microscopy (SEM, JSM-20, JEOL). X-ray diffraction (XRD) data were obtained under a diffractmeter equipped with a graphite monochromator using Cu K_α radiation.

Tensile strength of single filament was measured on a universal testing machine, using a gauge length of 25 mm and an extension rate of 0.2 mm/min. The diameter of the fiber was determined with a micrometer and the average tensile strength was obtained through 25 specimens.

4 RESULTS AND DISCUSSION

4.1 Correlation between air-curing process and oxygen content of PCS fibers

Air-curing conditions and the results are shown in Table 1. As the temperature rises and the keeping time increases, mass gain, gel content and reaction degree of Si-H bond were all increasing, but they behaved much differently. Fig. 1 illustrates the correlation of the three values.

In Fig. 1, mass gain is proportional to the reaction degree of Si-H bond. This can be easily understood that PCS reacts with oxygen as following:

$$2Si-H + O_2 \longrightarrow Si-O-Si + 2H_2O \quad (1)$$

Mass gain, Δm, is determined by the following:

$$\Delta m = \frac{\Delta M}{M_0} \times 100\% \quad (2)$$

While oxygen content, $w(O)_1$, has a relation with ΔM as follows (On the assumption that only oxygen enters the fiber body with no other mass changes, then, mass gain is just the oxygen increment.):

$$w(O)_1 = \frac{\text{oxygen-}(M_0)}{\text{overal-mass}(M_1)} = \frac{M_0^0 + \Delta M}{M_0 + \Delta M} = \frac{w(O)_0 + \Delta m}{1 + \Delta m} \times 100\% \quad (3)$$

Where $w(O)_0$ is oxygen content of the original fiber (green fiber), namely, 0.85%, which was recorded as run No. 0 in Table 1. Therefore, the mass

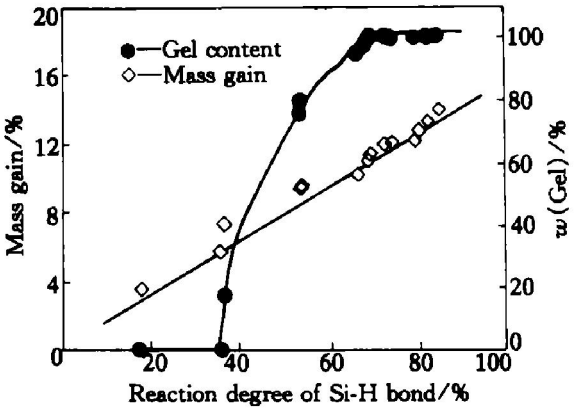

Fig. 1 Mass gain Δm and gel content behave differently with increase of reaction degree of Si-H bond

Table 1 Air-curing conditions and results

Run No.	Reaction temperature / ℃	Retaining time/ h	Δm / %	Reaction degree of Si-H bond/ %	Gel content/ %	$w(O)$ / %	
						Calculated	Measured
0	0	0	0	0	0	–	0.85
1	170	0	3.64	17.95	0	4.33	–
2	170	4	5.72	35.65	0	6.21	–
3	185	0	7.43	36.79	17.08	7.71	7.75
4	185	4	9.45	53.69	75.44	9.41	9.30
5	192	0	9.52	54.07	81.25	9.47	–
6	195	2	10.20	66.56	94.68	10.03	–
7	195	4	11.12	68.51	98.87	10.77	–
8	195	5	11.23	68.71	100	10.86	10.90
9	195	6	11.45	69.16	100	11.04	–
10	195	9	11.92	72.78	100	11.41	–
11	195	12	12.16	74.51	100	11.60	11.71
12	195	20	12.24	79.05	100	11.66	–
13	195	25	12.86	80.52	100	12.15	–
14	195	30	13.39	82.14	100	12.56	12.60
15	195	35	14.11	84.95	100	13.11	–

gains given, oxygen content of the cured fibers can be calculated from Eqn. 3. The specific data has been listed in Table 1.

Furthermore, oxygen contents of some samples have been measured and listed comparatively to the calculated ones. As shown in Table 1, the two data are in good agreement. Eqn. 3 is effective to calculate oxygen content from the mass gain of precursor fibers.

4.2 Correlation between pyrolysis process and oxygen content of SiC fibers

Pyrolysis is a conversion process from organic to inorganic. In the process, hydrogen and methane are evolved, as well as some trace of carbon monoxide.[4] Because the pyrolysis is going on under inert atmosphere and the evolved carbon monoxide can be ignored, oxygen of the fibers can be regarded as a constant mass during the pyrolysis. Then we can easily calculate oxygen content of SiC fibers from those of their cured PCS fibers.

Provided that no oxygen lost and increased during the pyrolysis process, oxygen mass is constant before and after pyrolysis, that is:

$$w(O)_1 \times m_1 = w(O)_2 \times m_2 \quad (4)$$

Therefore, $w(O)_2$, oxygen content of the ceramic SiC fiber, could be obtained with the data of $w(O)_1$, oxygen content of cured PCS fiber and σ_s, ceramic yield of the PCS fiber, as follows:

$$w(O)_2 = \frac{w(O)_1 \times m_1}{m_2} \times 100\% = \frac{w(O)_1}{\sigma_s} \times 100\% \quad (5)$$

From the data of $w(O)_1$ and σ_s listed in Table 2, $w(O)_2$ were obtained. However, the calculated data is not close to the measured ones. As a tendency, the real oxygen content is about 0.8% higher than the calculated value. This is mainly caused by the accumulated oxygen contamination from inert atmosphere that may contain some trace of oxygen. This viewpoint has ever been confirmed by the XPS analysis of SiC fibers with an oxygen rich surface[4].

Eqn. 5 is applicable if the inert atmosphere is purified enough. Even if not, the real values can also be approached from the calculated ones with addition of a constant (e.g., 0.8%). Therefore, a relationship between oxygen content of SiC fibers and mass gain of their precursor fibers can be established by the combination of Eqn. 3 and Eqn. 5.

$$w(O)_2 = \frac{w(O)_0 + \Delta m}{(1 + \Delta m)\sigma_s} \times 100\% + \text{const} \quad (6)$$

4.3 Correlation between oxygen content and tensile strength of SiC fibers

Correlations between oxygen content, tensile strength and density of SiC fibers are listed in Table 2 and illustrated by Fig. 2. They both show a peak at the oxygen content of 12% ~ 13%.

To analyze influence mechanism of oxygen content on the tensile strength of SiC fibers, we should firstly understand the purpose of oxidation. As mentioned above, air-curing is a crosslinking process and oxidation results in the Si-O-Si bridge, with an increase of gel content and ceramic yield. Then, based on this point, oxygen content should have a positive effect on the tensile strength and density

Table 2 Ceramic yield and oxygen content of SiC fiber

Run No.	Cured PCS fiber		SiC		Fiber	
	$w(O)$/%	σ_s	$w(O)$/%		Tensile strength/GPa	Density/($g \cdot cm^{-3}$)
			Calculated	Measured		
0	0.85	64.50	1.32	1.74	–	2.30
1	4.33	69.40	6.24	–	–	2.38
2	6.21	73.21	8.49	–	–	2.40
3	7.71	74.70	10.32	11.05	0.75	2.40
4	9.41	80.62	11.67	12.34	1.55	2.45
5	9.47	81.70	11.59	–	1.78	2.50
6	10.03	82.30	12.18	–	1.99	2.45
7	10.77	83.82	12.85	–	2.01	2.45
8	10.86	84.20	12.90	13.45	1.98	2.42
9	11.04	85.01	12.98	–	1.96	2.40
10	11.41	84.80	13.46	–	1.91	2.40
11	11.60	85.25	13.61	–	1.86	2.38
12	11.66	85.66	13.61	–	1.75	2.38
13	12.15	85.65	14.18	–	1.70	2.35
14	12.56	85.85	14.63	15.45	1.65	2.35
15	13.11	86.10	15.23	–	1.64	2.35

because it increases ceramic yield and decreases porosity. In Fig. 3, the ' ceramic yield' curve demonstrates this trend. With increase of oxygen content, the ceramic yield, as listed in Table 2, is truly rising.

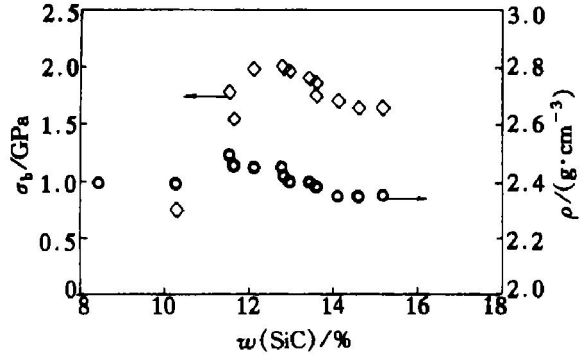

Fig. 2 Tensile strength and density of SiC fibers as function of oxygen content reveals peak value at about 12% ~ 13%, which corresponding to mass gain of 10% ~ 11% in curing

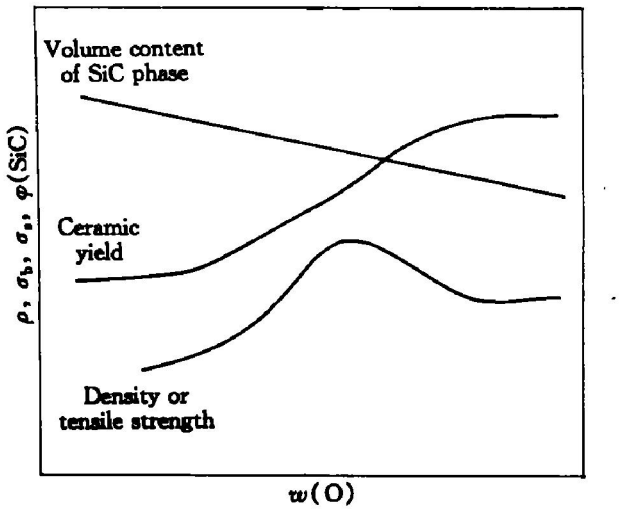

Fig. 3 Influence mechanism of oxygen content on tensile strength, with both effects of ceramic yield and volume content of SiC phase resulting in peak of tensile strength

Fig. 4 gives the surface and cross-section SEM images of SiC fibers. For the lower oxygen content SiC fiber, 11.05%, its ceramic yield is just 74.70% and pitting defects and cracks (pores) were frequently formed on the surface and cross-section. Therefore, its tensile strength is much reduced (0.75 GPa). On the contrary, a higher oxygen content of 13.45% gives both a higher ceramic yield of 84.20% and a higher tensile strength of 1.98 GPa, with its surface smooth and cracks smaller.

However, this is not always the truth. As shown in Fig. 2, too much oxygen content causes another reduction in tensile strength and density. Just simply take for granted that porosity is constant for the whole system regardless of their ceramic yield, then, the increase in oxygen content should always decrease the density of fibers. This is because the density of crystal (actually, oxygen is in silicon oxycarbide phase, SiC_xO_y [5]), 2.20 g/cm^3, is lower than that of SiC, 3.20 g/cm^3. This trend has been illustrated in Fig. 3 as ' volume content of SiC phase'. As dis-

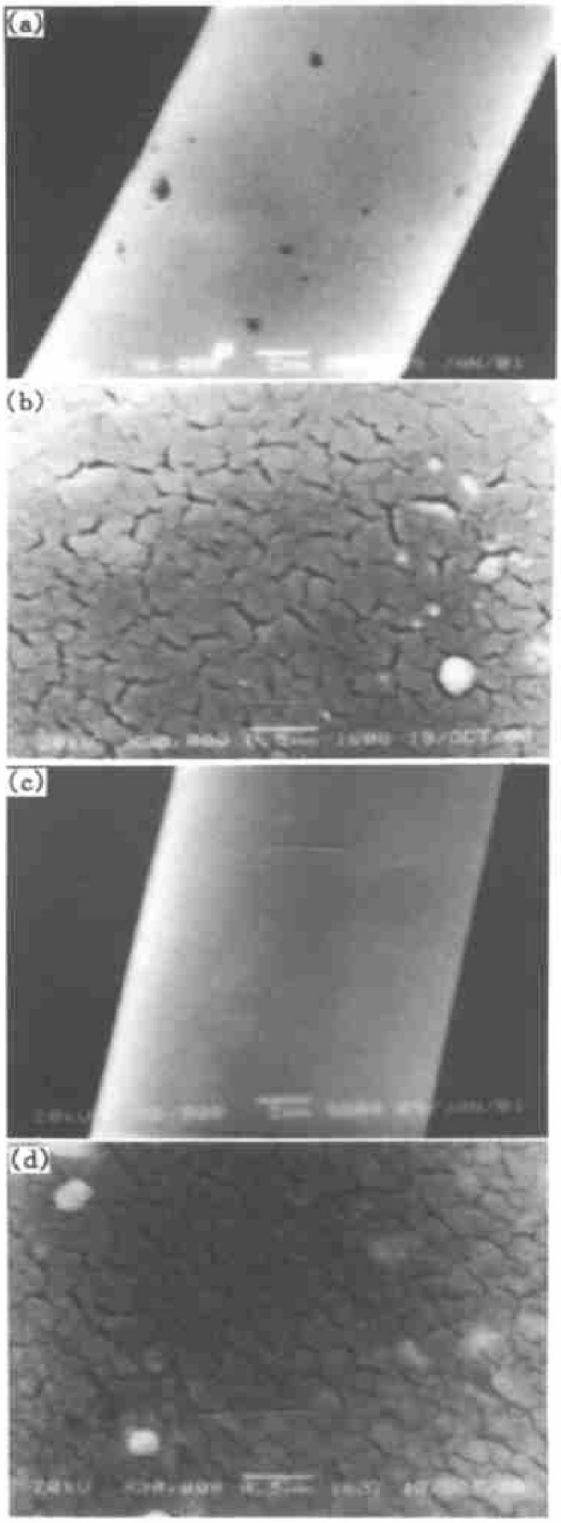

Fig. 4 Surface and cross-section SEM images of SiC fibers with oxygen content of 11.05% ((a) and (b)) and 13.45% ((c) and (d))

cussed above, the difference in porosity caused by the different ceramic yield could not be ignored; therefore, the equilibrium between these two effects gives another reduction in density, which reaches its peak value at the moderate oxygen content.

As far as the tensile strength is concerned, the density is indeed playing a role. But, the strength is more determined by the fiber microstructure. As being pointed out, excellent tensile strength could be only obtained for finely crystallized fibers given a fixed composition[12]. So, to reach a better strength, the fiber should be crystallized to a proper size, neither too large nor too small (amorphous).

However, as indicated by Fig. 5, the crystallization of β-SiC in the SiC fiber is inhibited by the increase of oxygen content. The fiber in Fig. 5(a), destroying fiber shape because of confusion in firing, has an oxygen content of 1.74% and shows clear diffraction peaks corresponding to β-SiC. With increasing oxygen content, the crystallization is much retarded. Up to 15.45%, the fiber becomes completely amorphous.

Considering all these effects, the tensile strength should have a peak value at the moderate oxygen content, 12% ~ 13%, similar to the behavior of density.

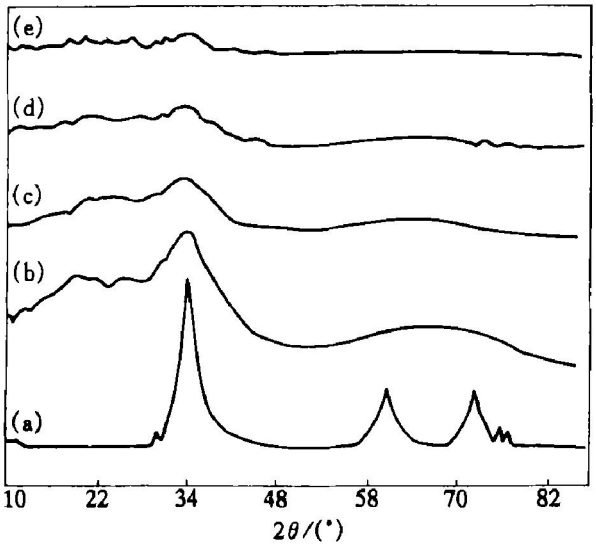

Fig. 5 XRD patterns of SiC fibers with oxygen content of 1.74% (a), 11.05% (b), 12.34% (c), 13.45% (d) and 15.45% (e)

5 CONCLUSIONS

1) Through curing and pyrolysis analysis, a mathematical relation is established between oxygen content of SiC fibers and mass gain of their precursor fibers. The equation is effective.

2) Oxygen content has a great influence on the mechanical properties, with a peak value at moderate oxygen content, 12% ~ 13%. So dose the density of SiC fibers.

3) Oxygen content is positive to the ceramic yield, and thus, good to the density and tensile strength; while, oxygen content is also negative to volume content of SiC phase and crystallization of SiC fiber, and thus, detrimental to the density and tensile strength. Both of these effects result in the peak behavior of the tensile strength of SiC fibers.

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