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Evolution of crystallization and its effects on properties during pyrolysis of Si–Al–C–(O) precursor fibers

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Abstract The high-temperature resistant Si–Al–C–(O) fibers were prepared through polymer-derived method using continuous polyaluminocarbosilane (PACS) fibers. Evolutions of the crystallization during the pyrolysis of the Si–Al–C–(O) precursor fibers were investigated by a series analysis. The structure of the fibers transforms from organic state to inorganic state and the crystalline phases appear during the pyrolysis. The β-SiC crystallite size increases when the temperature is higher than 1,300 °C. At the same time, the α-SiC appears. At 1,600 and 1,800 °C, the grain size of β-SiC of the fibers is 15.4 and 22.1 nm, respectively. The growth of β-SiC and the appearing of α-SiC have a great influence on the properties of the fibers. The change of the tensile strength of the pyrolysis products is divided into three stages with the growth of the crystal. The tensile strength of the Si-Al-C fibers is higher than 1.9 GPa.

Introduction

The high-temperature stability of SiC-based ceramics has led to their use in high-temperature structural materials and composites [1–3]. In particular, silicon carbide (SiC) fibers are used in tough fiber-reinforced composites. Since Yajima's synthesis of polycarbosilane (PCS) as precursor, polymer-derived SiC fibers have been extensively studied [2, 3]. Later, Nippon Carbon Company had produced commercial SiC fibers in 1982, which was named Nicalon fibers.

But, one problem of those fibers such as Nicalon is that thermo-mechanical stability is good only below 1,200 °C. The major mechanism of the thermal degradation of SiC fibers has been reported to be the oxidation of silicon and carbon [4, 5]. That forms volatile CO and SiO products, which results in large losses, formation of porosity, and the growth of SiC grains in the fibers. Of these factors, the increase of the SiC grains has a great harm on the properties of SiC fibers because it causes the structure of the fibers to loosen.

Recently, several attempts have been made with the objective of improving the mechanical properties and thermal stability of these fibers. One of the methods is to prepare near-stoichiometric SiC fibers by introducing small amount of heteroelement, such as aluminum or boron, into the precursor polymer [6]. For example, the temperature of continuous SiC fibers with Ti or Zr prepared by Ube Industries is about 1,500 °C. Lipowitz et al. had prepared continuous SiC fibers with Be, which also could be used at 1,500 °C. But these fibers with Ti, Zr, or Be still cannot meet the need in many places. In 1998, Ishikawa et al. [7] prepared the high-temperature resistant SiC fibers using polyaluminocarbosilane (PACS). The precursor PACS was synthesized from PCS and aluminum acetylacetonate ($Al(AcAc)_3$). The heteroelements of Al can restrain the increase of SiC grains at high temperature.

And as is known, the high-temperature properties of materials are significantly affected by the crystallization behavior, most of the studies about the SiC fibers with Al are focused on the properties and application of the fibers. And there are few on the mechanism of the preparation of the fibers. Therefore, the crystallization behavior of the fibers is worthy of a particular study.

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In this paper, the high-temperature resistant Si–Al–C–(O) fibers were prepared through polymer-derived method using continuous PACS fibers. Evolution of the crystallization during the pyrolysis of the Si–Al–C–(O) fibers precursor was investigated and the effect on the properties of the fibers was discovered.

Experimental procedure

Preparation of samples

Polysilocarbonsilane (PSCS) used as reagent was synthesized in our laboratory and the boiling point was about 190 °C. Al(AcAc)$_3$ was produced by Aldrich in USA, and the purity was 99%. The argon used as protection gas was produced in Changsha Jingxiang Corporation, and the purity was about 99.999%.

The precursor PACS was prepared by the reaction of PSCS with Al(AcAc)$_3$ above 300 °C in nitrogen gas at atmospheric pressure. The PACS was melted and spun into fibers composed of 200 continuous filaments with a multi-holes spinning machine in nitrogen [8]. The green fibers were then cured in air oven at a certain heating speed from the room temperature to 180–220 °C. The cured fibers were heated at 1,300 °C in argon atmosphere and then Si–Al–C–O fibers were obtained. The Si–Al–C fibers were obtained through sintering of Si–Al–C–O fibers at 1,800 °C in argon.

FT-IR spectroscopy

The powder samples were analyzed in the form of KBr pellets. Fourier Transform Infrared Spectra were collected in the range 400–4,000 cm^{-1} on Nexus 670 spectrophotometer. KBr discs were prepared by compressing a finely ground mixture of about 5 mg of samples and 300 mg of KBr powder.

X-ray diffraction

XRD was performed by a Siemens D-500 diffract meter (Germany) using nickel filtered copper $K\alpha$ radiation. The powder samples were prepared by crushing the samples with an agate mortar and pestle. The specimens were scanned over the 2θ range from 10 to 90°.

Scanning electron microscopy and transmission electron microscopy

The microstructure of the samples was examined using SEM (JSM-5600LV, JEOL, Japan, accelerating voltage 20 kV) and HRTEM (JEM-2010FEF, JEOL, Japan, accelerating voltage 200 kV). In the case of SEM, a thin layer of gold was coated on the samples.

Nuclear magnetic resonance spectroscopy

Solid-state NMR spectra of the samples were obtained on a Bruker AC-80 MHz spectrometer using standard Bruker magic-angle sample spinning (MAS) probes. ^{29}Si spectra were recorded by spinning powdered samples at 5 kHz using cross-polarization (CP) experiment.

Tensile strength test

The tensile strength of the samples was measured using a tensile testing machine (Model-YG-002, Taicang, China) with a gauge length of 25 mm at room temperature. The average tensile strength was obtained from the measured results of 25 filaments.

Results and discussion

Fourier transform infrared spectroscopy (FT-IR)

The wave numbers corresponding to the various absorption bands in the FT-IR spectra of the fibers (Fig. 1) are given in Table 1. These assignments are based on the reported data for PCS. The general features in the spectrum of PACS fibers appear similar to the published spectrum of the PC-470 type PCS [2, 3].

As shown in Fig. 1a, FT-IR indicates that the major bonds present are Si–CH$_3$ (1,250 cm^{-1}) and Si–H (2,100 cm^{-1})

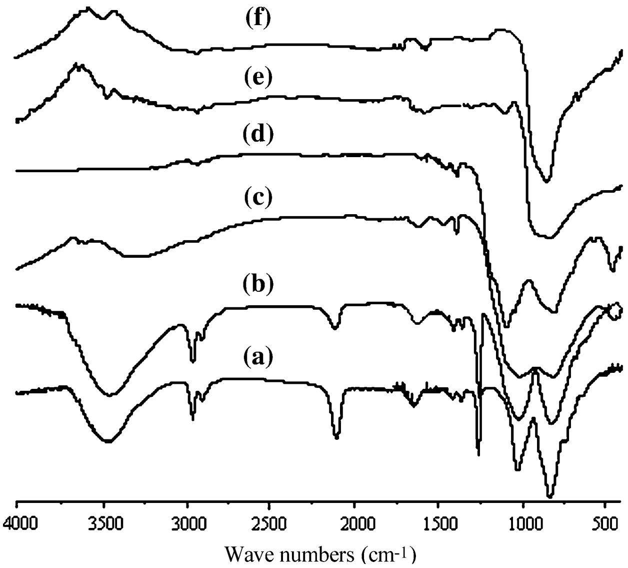


Fig. 1 FT-IR spectra of the cured PACS fibers and the products prepared at different temperatures in argon

Table 1 FT-IR absorption peaks and corresponding assignments to various groups

Wave numbers/cm^{-1}	Assignments
3400, 1640	O–H stretching in H_2O
2950, 2900	C–H stretching
2100	Si–H stretching
1410	C–H deformation in Si–CH_3
1360	CH_2 deformation in Si–CH_2–Si
1250	Si–CH_3 deformation
1020	CH_2 deformation in Si-CH_2–Si
1000–1100	Si–O stretching in Si–O–Si or Si–O–C
860–690	Si-CH_3 bending, Si–C stretching in SiC_4

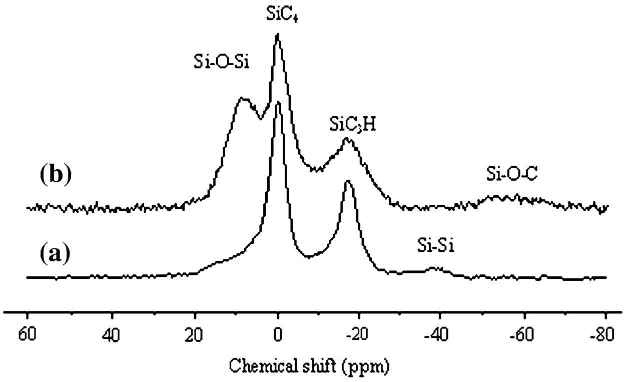


Fig. 2 ^{29}Si CP/MAS NMR spectra of PACS fibers and cured PACS fibers

in the PACS fibers. The broad band at around 1,020 cm^{-1} is due to the overlapping of CH_2 groups in Si–CH_2–Si units at around 1,020 cm^{-1} and Si–O bonds at around 1,080 cm^{-1}. The band at around 3,700 cm^{-1} may have been due to O–H stretching of Si–OH or water. Si–C (820 cm^{-1}) and Si–H (880 cm^{-1}) bonds may have contributed to the bands at around 800 cm^{-1}.

After air curing, as shown in Fig. 1b, the strong absorption peak centered at 1,099 cm^{-1} is attributed to Si–O stretching in Si–O–Si, which suggests the existence of oxygen in the cured PACS fibers. Si–H stretching (2,100 cm^{-1}), C–H stretching (2,950, 2,900 cm^{-1}), Si–CH_3 deformation (1,250 cm^{-1}), Si–CH_3 bending, and Si–C stretching in SiC_4 (690–860 cm^{-1}) [9, 10] can also be observed. But the intensity of Si–H stretching (2,100 cm^{-1}) becomes weak. This reduction is considered to be the reaction of Si–H bonds with oxygen [7].

When heat treated at elevated temperatures (1,000 and 1,300°C), as shown in Fig. 1c, d, the absorption peaks of Si–H stretching, C–H stretching, and Si–CH_3 deformation disappear. It indicates that the transition from organic state to inorganic state is essentially completed. When the temperature rises to 1,600°C (Fig. 1e) or 1,800°C (Fig. 1f), the Si–O stretching also disappears completely, and only the Si–C bonds (820 cm^{-1}) in the fibers can be observed. This implies that the oxygen is eliminated during the sintering of Si–Al–C–O fibers under argon.

Nuclear magnetic resonance (NMR)

The ^{29}Si CP/MAS NMR experiments were used for evaluating the silicon local coordination environments of the PACS fibers and the pyrolyzed products.

The ^{29}Si CP/MAS NMR spectra of the PACS fibers are given in Fig. 2a. It gives three separate resonance signals. The strongest peak with the maximum at 0 ppm is assigned to SiC_4 sites. The peaks at −16 ppm and −40 ppm are attributable to SiC_3H sites and Si–Si sites, respectively. As is shown in Fig. 2b, the peak at −16 ppm that is assigned to SiC_3H becomes weak and the peak at −40 ppm that is assigned to Si–Si bonds disappears after air curing. At the same time, there appears two peaks at +8 ppm and −55 ppm, which are assigned to Si–O–Si and Si–O–C phases, respectively.

The ^{29}Si CP/MAS NMR spectra of the pyrolyzed products obtained at different temperatures in argon are shown in Fig. 3. The resonance peak centered at −14.7 ppm and the shoulder at around −18.7 ppm, as shown in Fig. 3a, is assigned to ordered and disordered *β*-SiC, respectively. In addition, the SiC_3O resonance (0 ppm) is believed to be hidden by the broad peak at −14.7 ppm in the spectrum of the Si–C–O–Al fibers. The resonance peaks at −32, −72, and −107 ppm are assigned to the SiC_2O_2, $SiCO_3$, and SiO_4 phases, respectively. In Fig. 3c, the peaks at −15.9, −19.9, and −24.7 ppm are assigned to ordered *β*-SiC, disordered *β*-SiC, and *α*-SiC, respectively.

By comparing the three spectra in Fig. 3, there is also a slight upfield chemical shift of ordered *β*-SiC (from −14.7

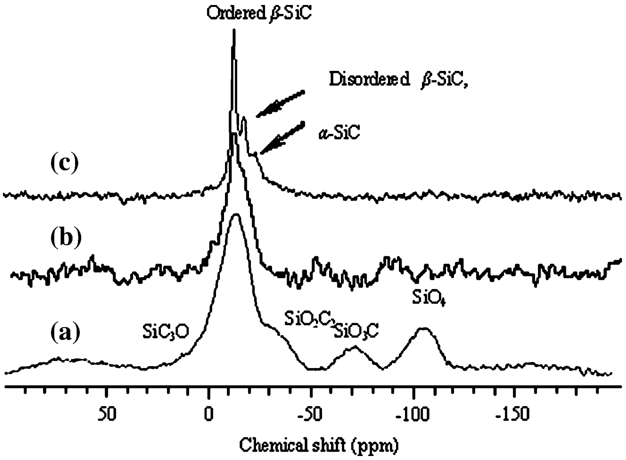


Fig. 3 ^{29}Si CP/MAS NMR spectra of the pyrolysis products obtained at different temperatures in argon of cured PACS fibers

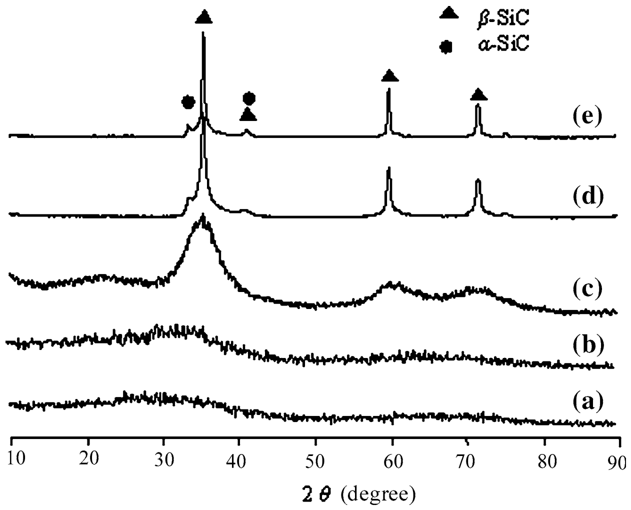


Fig. 4 X-ray diffraction (XRD) patterns of the cured PACS fibers and the products prepared under different temperatures in argon

Table 2 The average grain size of β-SiC crystalline of the pyrolyzed products

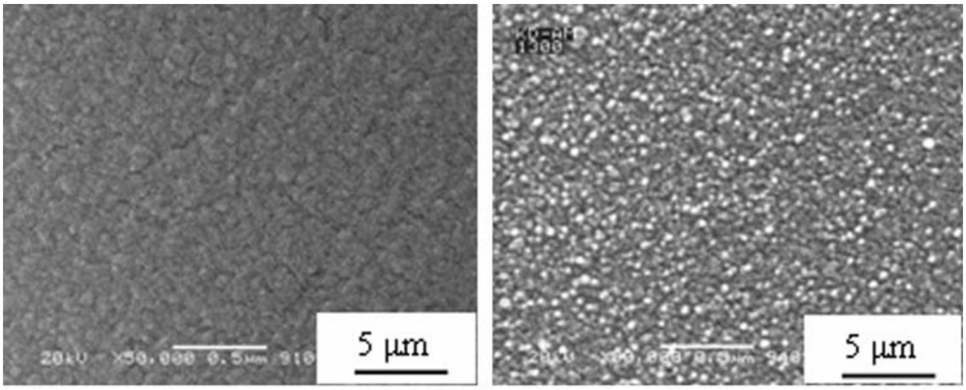
Temperature (°C)	1000	1300	1400	1500	1600	1700	1800
The average grain size of β-SiC (nm)	≈0	1.8	2.1	7.2	15.4	20.4	22.1

to −15.9 ppm). The upfield chemical shift is presumably caused by a deprotonation reaction occurring at the carbon sites with silicon sites. The shift could also be related to an ordering of the various sites. Considering this fact, it can be concluded that the SiC_xO_y and SiO_4 phases in the Si–C–Al–O ceramic fibers are removed with the increase of temperature. The amount of the ordered β-SiC increases during the sintering of Si–Al–C–O fibers. In addition, a small amount of α-SiC is detected in the samples prepared at 1,800 °C.

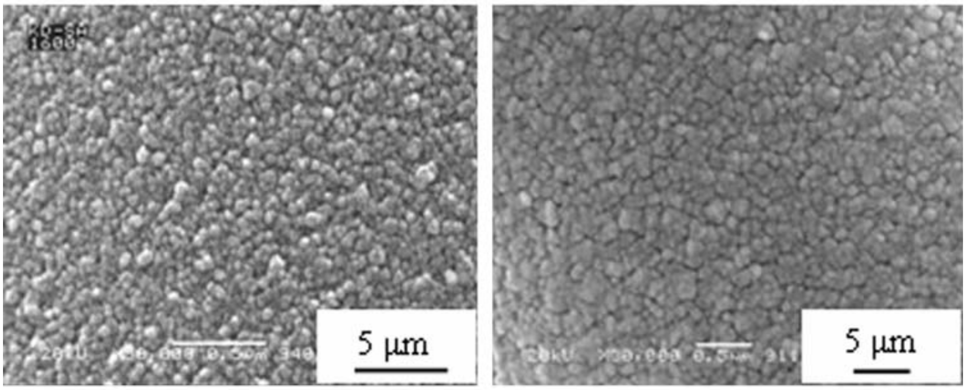
X-ray diffraction (XRD)

The powder X-ray diffraction peaks of cured PACS fibers and the pyrolyzed products at different temperatures in argon are shown in Fig. 4. It can be found clearly that there is no peak in the XRD patterns of the cured PACS fibers. With the increase of temperature, β-SiC at $2\theta = 36.5°$ is observed. This peak in the fibers prepared at 1,000 °C is broad and weak. It indicates that the fibers prepared at 1,000 °C have an amorphous structure [10–12]. The peak at $2\theta = 36.5°$ becomes sharp at 1,300°C. At the same time, there appear two weak peaks at $2\theta = 61.0°, 72.0°$ corresponding to β-SiC grains. In Fig. 4d, e, the peaks at $2\theta = 36.5°, 61°, 72°$ become very sharp, indicating a high

Fig. 5 SEM images of cured PACS fibers and the pyrolyzed products



(a) Cured PACS fiber
(b) 1300 °C



(c) 1600 °C
(d) 1800 °C

crystalline structure. There also appears α-SiC grains at $2\theta = 34.1°$, 41.3° [13, 14]. This is consistent with the NMR results for the Si–C–Al fibers, which shows the peaks (−24.7 ppm in the ^{29}Si CP/MAS NMR) assigned to α-SiC.

It is well known that the crystallization of material is strongly affected by the purity, surface quality, atmosphere, temperature, etc [15, 16]. Generally, the crystallization mechanism of SiC fibers is surface nucleation and growth, and the initial crystallization temperature decreases with the increase of specific surface area and impurity. Table 2 is the average grain size of β-SiC of the fibers pyrolyzed at different temperatures. It can be known that the average grain size of β-SiC increases with the increase of temperature. The size of β-SiC grows rapidly when the temperature is higher than 1,400 °C. It indicates that the effect of temperature is high on the crystallization of the fibers. The size of β-SiC in the Si–Al–C fibers is about 22.1 nm.

Scanning electron microscope (SEM)

The SEM images of the cured PACS fibers and the pyrolyzed products in argon are given in Fig. 5. As shown in Fig. 5a, no SiC grains are observed on the surface of the cured PACS fibers. SiC grains appear on the surface of the fibers prepared at 1,300 °C. But the grains are very small. When the temperature is higher than 1,300 °C, the grains on the surface of the fibers become bigger with the increase of temperature, as shown in Fig. 5c, d. This implies that there is a transformation from amorphous state to crystal state during the pyrolysis of the precursor fibers.

High-resolution transmission electron microscope (HRTEM)

Figure 6 is the HRTEM observations of continuous Si–Al–C–O fibers and the products heated at different temperatures in argon. The sample prepared at 1,300 °C shows clear phase separation between the crystalline phase and the amorphous phase [17]. The lattice distance of the crystalline phase is 0.25 nm, which is assigned to 111 plane of β-SiC. It indicates that the fiber is composed of β-SiC and amorphous phase. But the area of β-SiC crystalline is very small and distributes among the amorphous phase.

The sample prepared at 1,600 °C shows that the fibers are composed of β-SiC crystalline mostly. The lattice distance of the crystalline phase is 0.25, 0.21, and 0.13 nm, which are assigned to 111, 200, and 311 planes, respectively, of β-SiC. The size of β-SiC is bigger than that of the sample prepared at 1,300 °C. Fast growth of SiC grains

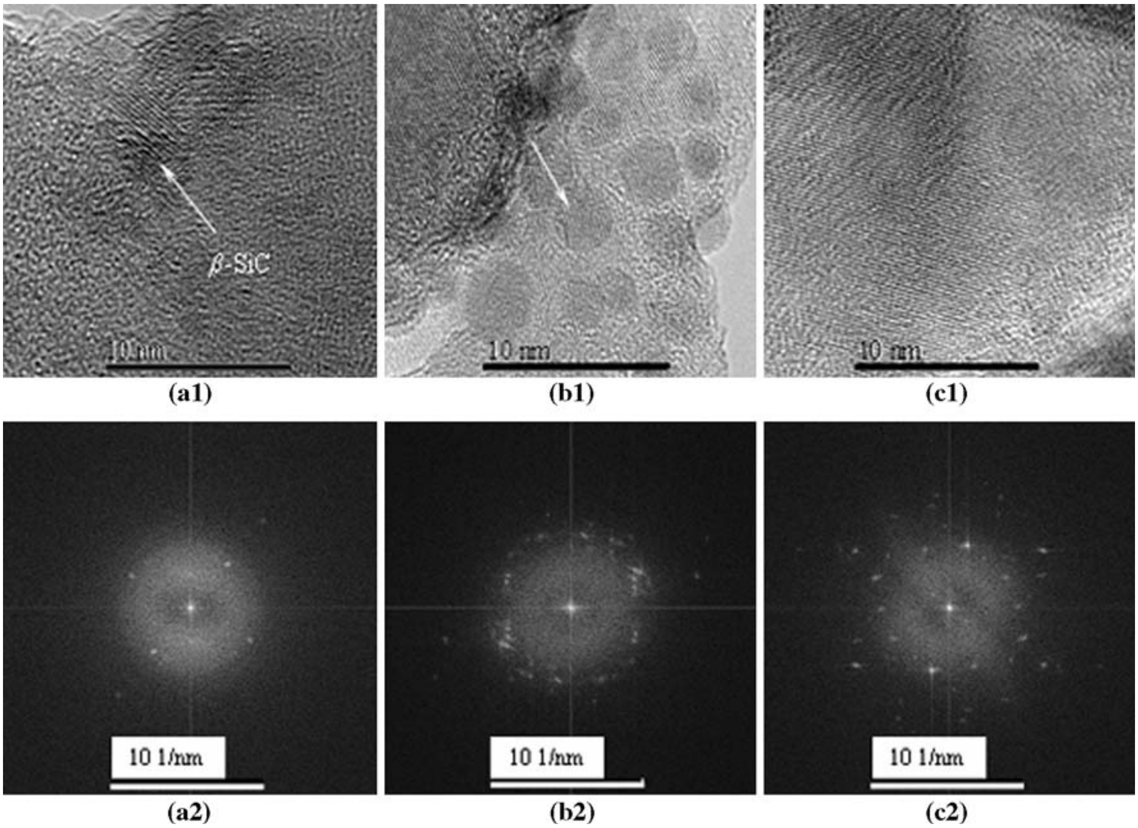


Fig. 6 HRTEM observations of continuous Si–Al–C–O fiber and the products pyrolyzed at different temperatures in argon

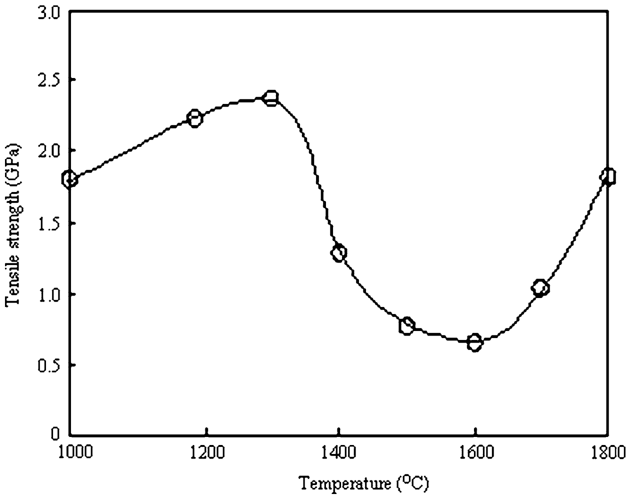


Fig. 7 Tensile strength of the fibers pyrolyzed at different temperatures in argon

occurs at 1,600 °C (see white arrow for crystal growth in Fig. 6b1).

There appears polytypic SiC in the sample prepared at 1,800 °C, including β-SiC and α-SiC such as 2H, 4H, 6H, and 15R [18] (Fig. 6c1, c2). The Si–Al–C fibers are composed of SiC completely.

Tensile strength

The tensile strength of the fibers pyrolyzed at different temperatures in argon is shown in Fig. 7. The change of the tensile strength is divided into three stages. Firstly, the tensile strength increases with the increase of temperature. It has the highest tensile strength at 1,300 °C. Secondly, the tensile strength decreases when the temperature was higher than 1,300 °C. It has the lowest tensile strength at 1,600 °C. It is found that the reason for the decrease in tensile strength is the formation of porosity with the growth of crystallization and the volatile of CO and SiO during the pyrolysis process. Thirdly, the tensile strength increases again when the temperature is higher than 1,600 °C. The element of aluminum plays a very important role as a sintering aid and makes the density of the fibers to increase [7, 19].

Conclusions

The high-temperature resistant Si–Al–C–(O) fibers were prepared through polymer-derived method using continuous PACS fibers. Evolutions of the crystallization during the pyrolysis of the Si–Al–C–(O) fibers precursor were investigated and the effect on the properties of the fibers was discovered. The cured PACS fibers, which exhibits an amorphous state, transforms from organic state to inorganic state during the pyrolysis process. The β-SiC grains of the pyrolysis products appear at 1,300 °C and it grows with the increase of temperature. The α-SiC appears at 1,600 °C. Temperature is an important factor that affects the crystallization of Si–Al–C–(O) fibers. The change of the tensile strength of the pyrolysis products is divided into three stages with the growth of the crystal. The crystallization behavior has a great influence on the properties of the fibers.

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