FULL PAPER

Crystalline structure in SiC fibers driven by pyrolysis temperature and time

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In this work, we study the impact of pyrolysis temperature and time on the crystalline structure of lab made silicon carbide (SiC) fibers and their mechanical properties. The polycrystalline structure and the characteristic length scales of β -SiC in fibers were characterized with X-ray diffraction, transmission electron microscope and synchrotron small angle X-ray scattering. The sizes of crystallites, particles and interparticle distance all increase as pyrolysis temperature or time increases while the crystallinity nearly remains constant, indicating SiC crystals in the fiber grow by absorbing the surrounding small crystals. The crystal growth follows the Ostwald ripening when pyrolysis temperature reaches 1500°C. At this temperature, longer pyrolysis time seems to reduce the tensile strength, but still keep increasing the modulus. The stiffness is possibly associated with the growth of particle size, interparticle distance and the size of voids in fibers.

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1. Introduction

Silicon carbide (SiC) fibers have exhibited superior mechanical properties at high temperature.^{1)–4)} The fiber reinforced composite (SiC_f/SiC) has many potential applications in energy fields including nuclear reactor due to its excellent thermal and radiation resistance.^{5),6)}

There are several approaches to synthesize SiC fibers including chemical vapor deposition, activated carbon fiber conversion and precursor melt-spinning process. Among them, the precursor method which was invented by Professor Yajima of the University of Northeastern University in 1975 is most popular due to its advantages in low production costs, high production efficiency, suitable for industrial production.⁷⁾ SiC fibers produced in this method has been developed to the third generation, in which the crystallinity is the highest among all generations and the mechanical performance is the best.⁸⁾

Our SiC fibers are generation II fibers. Previous research have indicated that in this type of fiber there are β -SiC crystallites as well as amorphous Si-C-O.⁸⁾ The manufacturing conditions including pyrolysis temperature and time duration directly affect the microstructure of the fiber and hence the performance of it.⁹⁾ Previous research has mainly focused on the structure analysis on the finished

fibers,^{10),11)} or the thermal stability of them.^{3),12)} There is no report of systematic research on the effect of curing conditions on the crystalline structure of SiC fibers so far. In this work, we study the effect of pyrolysis temperature and time on the crystalline structure of SiC fibers at nanoscale. Previous reports on the scale of crystalline structure have focused on the size of β -SiC particles.¹³⁾ In our work, we measure the size of the β -SiC crystallites, polycrystalline SiC particles composed of crystallites and the interparticle distance by methods of X-ray diffraction (XRD), transmission electron microscope (TEM) and small angle X-ray scattering (SAXS) respectively. SAXS is known to obtain the information about the size of the particle and interparticle distance at around 1 to hundreds of nanometers.^{14),15)} To the authors' best knowledge, this statistical information of the average interparticle distance in fiber has never been reported. Our work provides an overall picture of SiC crystals in the fiber. The evolution of the SiC structural length scale driven by pyrolysis temperature and time duration is discussed and compared with the change of the mechanical properties.

2. Experimental and methods

The SiC fibers were fabricated by the method of precursor melt-spinning process. The polycarbosilane (PCS) precursors were irradiated with electron beam in inert gas at room temperature, and then pyrolyzed at 1000°C to obtain primitive SiC fibers. These primitive SiC fibers were pyrolyzed again at different high temperature points (1200, 1300, 1400, 1500°C) in order to convert them into

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freestanding SiC fibers. The as-obtained SiC fibers are hereinafter referred to A series as of A-1, A-2, A-3 and A-4, respectively. Another group of SiC fiber samples referred to B series in total number of 9 were irradiated with three length of time duration (80, 120 and 240 s) during pyrolysis treatment at three different temperature points: 1300, 1400, 1500°C.

The tensile strength and tensile modulus of SiC fibers were tested with Electromechanical Materials Testing System (Instron model 5940) following standard GB/T 3362-2005.¹⁶⁾ The result is the average of six specimens for each property test.

XRD patterns were recorded using a Bruker D8 Advance diffractometer with a Bragg–Brentano geometry with a CuK α radiation ($\lambda = 1.5418 \text{ \AA}$) in the diffraction of 2θ from 5 to 90 deg. at a tube voltage of 40 kV and a tube current of 40 mA.

TEM experiment were conducted using a FEI Tecnai G2 S-TWIN (accelerating at 200 kV) microscope.

SAXS measurement was performed on beamline BL16B1 using a three-slit system at Shanghai Synchrotron Radiation Facility (SSRF). An energy resolution of 6×10^4 was obtained from a water-cooled Si (111) double-crystal monochromator. The wavelength of the X-ray was 0.124 nm. The 2D SAXS patterns were recorded by a Mar165 CCD at a resolution of 2048×2048 pixels and a pixel size of $80 \mu\text{m} \times 80 \mu\text{m}$ for quantitative analysis. The sample-to-detector distance was 1920 mm for SAXS (calibrated by beef tendon standard). This setup would obtain scattering vector Q in a range of $0.09\text{--}1.8 \text{ nm}^{-1}$, corresponding to a probing scale of 3–70 nm in real space.

Samples of SiC fibers were measured during SAXS experiment as fiber itself and ground powder respectively. For fiber test, a bunch of fibers were placed vertically so that the beam is perpendicular to the axis of fiber. For powder test, the fibers were ground into powder and hold by scotch tape, as Fig. S1 shows.

3. Results

3.1 Properties of samples

The average bulk compositions of SiC fibers were measured by chemical element analysis are shown in **Table 1**. Irradiation of PCS by electron beam in an inert atmosphere followed by pyrolysis results in ceramic fibers with a low oxygen content of $\sim 1 \text{ at\%}$. Due to the low concentration of oxygen in the fibers, it is expected that there is nearly no Si–C–O amorphous phase in the material. The tensile strength for A-1, A-2, A-3 and A-4 are 1.98, 2.22, 2.30 and 2.43 GPa, respectively.

Table 1. Chemical analysis and tensile properties of SiC fibers

Sample	Chemical analysis [at%]			Chemical formula	Ten. strength [GPa]	Ten. modulus [GPa]
	C	Si	O			
A-1	58.94	39.88	1.18	SiC _{1.48} O _{0.030}	1.98 ± 0.1	171 ± 2.6
A-2	58.53	40.14	1.33	SiC _{1.46} O _{0.033}	2.22 ± 0.08	180 ± 3.6
A-3	56.98	41.91	1.11	SiC _{1.36} O _{0.027}	2.30 ± 0.05	196 ± 4.0
A-4	57.77	41.05	1.18	SiC _{1.41} O _{0.028}	2.43 ± 0.12	203 ± 1.8

2.22, 2.30 and 2.43 GPa, respectively. The tensile modulus for A-1, A-2, A-3 and A-4 are 171, 180, 196 and 203 GPa, respectively. It was found that that the tensile strength and modulus increases as the pyrolysis temperature increases, and the pyrolyzed temperature can play an important role in the mechanical properties of the SiC fiber.

3.2 SiC crystallite size-XRD

As shown in **Fig. 1**, the XRD patterns suggests the crystals in fibers are β -SiC with three major peaks (111), (220) and (311) that can be detected. From A-1 to A-4, as pyrolysis temperature increases, the diffraction peaks become sharper and the intensities increase, indicating the increase of crystallinity in samples. Based on the XRD results, the size of SiC crystallites D and fiber crystallinity can be estimated, as seen on Fig. S2. Scherrer equation as shown below is used to determine the crystallite size:

$$D = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

where K is scherrer constant, λ is wavelength of X-ray, β is the FWHM and θ is the diffraction angle. Here $k = 0.94$ as β -SiC is spherical crystals with cubic symmetry.¹⁷⁾ Here we take the average value calculated from the three major peaks. For A-1, A-2, A-3 and A-4 the crystallite size are 2.5, 2.7, 3.4 and 4.4 nm, respectively, increasing as pyrolysis temperature goes up.

We estimate the crystallinity via two different approaches. In one way we analyze the XRD curves by separating the crystalline diffraction from the amorphous scattering with the help of the DIFFRAC.EVA V.3.0 by Bruker. After the subtraction of the background and the integration to obtain the area under the amorphous curve and the total diffraction curve, the crystallinity of the sample is calculated by:

$$\text{Crystallinity} = \frac{\text{total area} - \text{amorphous area}}{\text{total area}} \times 100 \quad (2)$$

Fig. 1. XRD patterns of ground samples of A series and SiC powder as standard. The curves were shifted vertically for distinction.

From A-1 to A-4, the values of crystallinity are 80.6, 82.6, 86.4 and 86.5%, respectively. The result is consistent with previous reported values.¹⁸⁾

On the other hand, we compare the XRD patterns of the ground fiber and the standard β -SiC nanoparticles, as seen in Fig. 1. The area under the peaks marked by the dash line are calculated and by comparing the total peak area of each sample to the standard, we can obtain the crystallinity of samples in unit of volume percentage.

The results are 63.3, 63.5, 66.0 and 66.7% for A-1 to A-4. Taking into account of the density of our SiC fibers which are around 2.57 g/cm³, the crystallinity of our fibers in unit of weight percentage are 77.8, 78.1, 81.2, 82.0% respectively. Considering the uncertainty of the crystal-amorphous separation, this result agrees quite well with the first method. So we can conclude that the crystallinity of our SiC fibers are around eighties in weight percentage or sixties in volume percentage.

3.3 SiC particle size-TEM

The average crystalline particle size, L , of A series were measured under TEM. The result is summarized in Table 2. For A-1, A-2, A-3 and A-4 these values are 5.7, 6.3, 9.1 and 11.9 nm, respectively, increasing as pyrolysis temperature goes up, as shown in Fig. 2 (The enlarged TEM image were shown in Fig. S3). The average particle size of β -SiC particles, L is much larger than the size of crystallites, D determined by XRD. Estimated by the ratio $(L/D)^3$, each β -SiC particle is composed of 10–20 crystallites in average, depending on the pyrolysis temperature.

Table 2. Structural scale of β -SiC particles and crystallinity in SiC fibers

Sample	Crystallite Size D [nm]	Particle Size L [nm]	Domain #/ Particle $(L/D)^3$	Crystallinity [%]
A-1	2.5	5.7	12	63.3
A-2	2.7	6.3	13	63.5
A-3	3.4	9.1	19	66.0
A-4	4.4	11.9	20	66.7

Fig. 2. Average particle size of A series as a function of pyrolysis temperature points. Insets show the typical TEM images accordingly.

The higher pyrolysis temperature, the more crystallites in one single particle. The size values of crystalline structure characterized by XRD and TEM were summarized in Table 2.

3.4 Interparticle distance-SAXS

The 2D SAXS patterns of the A series in form of fiber and powder were shown in Fig. S4. After circular integration and air subtraction with Fit2D,¹⁹⁾ the corresponding scattering profile $I(Q)$ vs. Q were shown in Fig. 3. Each of the scattering curves was multiplied by an individual factor for easier observation of a hump on the curve, which is present in Q range of 0.2–1.2 nm⁻¹. The position of the humps for each sample is consistent between fiber and powder, and it systematically shifts to the lower Q as pyrolysis temperature goes up. This signal indicates the existence of strong scattering from electron density variation in the sample, which results in the halos on the 2D scattering images as seen in Fig. S4. Though some of the halos are hard to distinguish from the background scattering, their existence can be unveiled from the hump on the integrated scattering curve in Fig. 3. This signal is attributed to the scattering contrast between SiC crystals and the amorphous (mostly amorphous carbon) part in the fiber. Hence the average interparticle distance between two SiC particles can be roughly estimated from the peak position Q by $S = 2\pi/Q$. The value of S for A-1, A-2, A-3 and A-4 are 6.9, 9.7, 14.7 and 20.8 nm, respectively. Previous work by Suzuya et al.¹⁸⁾ also reported this diffraction peak and the increase of the corresponding real space scale as heat-treatment temperature went up. Their values coincided well with ours comparing the samples at the same treating temperature. However, they thought the SiC crystals were densely packed in the fiber and this interparticle distance can be estimated as the size of particle itself, even though the crystallinity of their samples are roughly same as ours, 60s in percentage. Based on our TEM observation, the size of the particles is distinctly smaller than the interparticle distance. This is also the first report on the interparticle distance in SiC fiber to the authors' knowledge.

4. Discussion

Figure 4(a) shows the evolution of three major scales driven by temperature. As pyrolysis temperature increases, β -SiC crystallites grow, and so does the β -SiC particles composed of the crystallites. However the growth speed of the particles is higher than the crystallites, so the average number of crystallites that each particle owes also increases, especially when temperature goes above 1400°C, as seen in Fig. 4(b). Taking into account of the fact that the crystallinity does not change much [see Fig. 4(b)], one can conjecture that the β -SiC particles coarsen by gathering the crystals around. This would directly lead to the increase of the interparticle distance, which was actually observed by our SAXS result and the values are shown in Fig. 4(a). If the particles were uniform in size, it would be easy to estimate the crystallinity by $(L/S)^3$. This value for the A

Fig. 3. Scattering intensity profile I vs q for fibers (a) and power (b) after the air scattering background was subtracted and 2D data was averaged circularly. The insets show the original scattering data with background signal (air).

Fig. 4. The structural and mechanical properties changes of A series SiC fibers. The crystalline structure at nano-scale for samples (a), Number of crystallite per particle (green triangle) and crystallinity (purple square) (b) and the tensile strength (square) and tensile modulus (triangle) (c) as a function of pyrolysis temperature. Schematic showing the evolution of crystalline structure under increasing pyrolysis temperature (d).

samples would be 56, 27, 24 and 19% as pyrolysis temperature goes up. This deduction is quite different with the XRD measurement result which shows the crystallinity

is at sixties in percentage. So the only reason that the particle size and the interparticle size do not increase proportionally is because the size distribution of the parti-

Fig. 5. The structural and mechanical properties changes of B series SiC fibers. Crystallite size (a), Particle size (b), Interparticle distance (c) and the tensile strength and tensile modulus (d) as a function of pyrolysis temperature.

Fig. 6. Fitting of crystal size with Ostwald Ripening formula for SiC fibers pyrolyzed at three temperature points.

cles are quite wide. In other words, as temperature goes up, many SiC crystals grow larger, but there are also some much smaller crystals in the fiber. The evolution of this crystalline structure change was pictured in Fig. 4(d). As the size of crystalline structure grows, the mechanical properties also improves, as seen in Fig. 4(c).

We also characterized the crystalline structure of SiC fibers referred to B series which were pyrolyzed at three time duration (80, 120, and 240 s) and temperature points (1300, 1400, 1500 °C). The results are summarized in Fig. 5. The size of crystallites, particles and interparticle distance all increase monotonously as pyrolysis temperature or time duration increases.

Crystal growth in many cases follow the Ostwald ripening rule where the volume of the crystal increases proportionally to the time:^{20),21)}

$$R^3 - R_0^3 = Kt \quad (3)$$

where R is the size of the crystal and t is the time. K is a temperature dependent parameter and R_0 is the starting size. Hence we try fitting the samples treated at the same temperature with this formula. Fitting result (see Fig. 6) shows the correlation coefficient is closest to 1 for samples treated at 1500 °C. The β -SiC crystallites size of SiC fibers which obtain at 1200, 1300, 1400 and 1500 °C are 2.5, 2.7, 3.4, and 4.4 nm, respectively. It can be seen that from 1200 to 1300 °C, the crystal size of SiC will almost not change. However, when the temperature reaches 1400 °C, its crystal size will increases slowly, and the temperature reaches 1500 °C, its crystal size will grow rapidly. It suggests that only when the pyrolysis temperature reaches 1500 °C will the growth of β -SiC follow the Ostwald ripening mechanism.

ism and only in this temperature the crystal size will grow rapidly.

The mechanical performance is different [Fig. 5(d)]. In general the tensile strength and modulus increases as the pyrolysis temperature increases which will due to the size of crystallites and particles increases, which is consistent with the behavior of A series. However their correlation with pyrolysis time is not monotonous. At 1400°C the longest duration time (240 s) produces fiber with the highest strength and modulus. At 1500°C 240 s pyrolysis time seems to slightly reduce the tensile strength while keep increasing the modulus, which means the material stretches less before it fractures. The reason that the fiber becomes stiffer is related to the structural change. The stiffness of the fiber is a result of the combinational effect among the crystalline structure, the amorphous phase, and a small amount of voids which also grow larger in size as increasing temperature.¹⁸⁾ And the amount of voids maybe increase and the size of voids maybe grow larger with the increase of duration time. The drop of the tensile strength is possibly related to the growth of the voids in the fiber.¹⁸⁾ Although the increases in the size of crystallites and particles increases with the increase of duration time, which will causes an increase in the tensile strength. So, we conjure that the growth of the SiC particle size, the interparticle distance and the consequent reshaped interface between the crystalline and amorphous contribute to this change.

5. Conclusion

We studied the structural changes associated with the mechanical properties of lab made SiC fibers pyrolyzed at various temperature points and with different time durations. The polycrystalline structure and the characteristic length scales of β -SiC crystals in the fibers were determined with various methods including XRD, SAXS and TEM. The results indicated that SiC crystals in our fibers are mostly polycrystals composed of 10–20 smaller crystallites in size of 2–5 nm, and the particles are around 7–20 nm apart in average, depending on the treating temperature and time. As the pyrolysis temperature goes up, the crystallinity of the fiber nearly remains constant while the size of the SiC particles goes up, leading to the increase of the interparticle distance. This structural change discloses that the SiC crystals in the fiber grow by absorbing the surrounding small crystals. The tensile strength and modulus increase as the pyrolysis temperature increases, while their correlation with pyrolysis time is not monotonous. The crystal growth follows Ostwald ripening

mechanism at 1500°C and the fiber also becomes stiffer at this temperature, associated with the growth of particle size, interparticle distance and size of voids in fibers.

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