J Mater Sci (2010) 45:5749–5755
DOI 10.1007/s10853-010-4645-7

Decarbonization mechanisms of polycarbosilane during pyrolysis in hydrogen for preparation of silicon carbide fibers

**Xueyuan Tang · Li Zhang · Huibin Tu ·
Hui Gu · Lifu Chen**

Received: 15 March 2010 / Accepted: 21 May 2010 / Published online: 8 June 2010

Abstract Polycarbosilane (PCS) fibers are cured by electron beam irradiation in helium. Then, the cured fibers are pyrolyzed under hydrogen. The mechanisms of carbon removal during pyrolysis are investigated using chemical elemental analysis, FTIR, Raman, and AES analysis. The development of microstructure and phase is examined by SEM, TEM, and XRD. The results show that the thermal cleavage of relatively weak Si–H and Si–CH_3 bonds takes place first during pyrolysis in hydrogen, generating free radicals. The free radicals then react with C–H bonds or with each other to form Si–CH_2–Si groups, releasing hydrogen and methane. As temperature increases, the Si–CH_2–CH_2–Si groups in PCS begin to dissociate and react with hydrogen to form methane, resulting in the further removal of carbon and giving silicon-rich silicon carbide fibers (i.e. C/Si <1).

Introduction

Fine diameter SiC-based fibers are produced via polycarbosilane (PCS) route on the base of the method developed by Yajima et al. [1–4]. The processing includes the synthesis of PCS precursor, melt-spinning to obtain precursor fibers, curing to render the fibers infusible, and finally pyrolysis to give silicon carbide fibers. Nicalon® is the representative of the first generation silicon carbide fibers. Because the precursor fibers are oxidation-cured, Nicalon® contains about 10 wt% oxygen, limiting its long-term service temperature below 1100 °C. Hi-Nicalon® is the second generation SiC fibers. The precursor fibers are cured by electron-beam irradiation in inert atmosphere, so that the oxygen content in Hi-Nicalon® is reduced below 1 wt%. However, Hi-Nicalon® contains about 20% excess carbon apart from silicon carbide. Therefore, its service temperature is only about 1300 °C. To further improve the thermal stability, the excess carbon must be removed to give near stoichiometric silicon carbide fibers. The third generation of silicon carbide fibers, Hi-Nicalon Type S®, has thus been developed [5, 6]. Hi-Nicalon Type S® is produced following essentially the same techniques as Hi-Nicalon®. However, the pyrolysis has been carried out in hydrogen instead of nitrogen. The hydrogen atmosphere affects the pyrolysis mechanisms, favoring the formation of methane (CH_4) rather than hydrogen (H_2) gas as in the case of Hi-Nicalon®. Methane takes more carbon away from the fibers, resulting in the formation of near-stoichiometric silicon carbide fibers when the pyrolysis conditions are optimized. Near-stoichiometric means that the C/Si ratio in the final ceramic fibers is 1.01–1.1. The long-term service temperature of Hi-Nicalon Type S® is estimated to be above 1450 °C.

Irrespective of the excellent properties of Hi-Nicalon Type S® fibers, only limited information has been published on the processing technology and especially the decarbonization mechanisms. Takeda et al. [7] have prepared silicon carbide fibers with C/Si ratio ranging from 0.84 to 1.56 by heating electron beam-cured PCS fibers in hydrogen-containing atmosphere. When the pyrolysis

X. Tang
College of Chemistry and Chemical Engineering,
Xiamen University, Xiamen 361005, China

X. Tang · L. Zhang · H. Tu · L. Chen (✉)
Advanced Materials Laboratory, College of Materials,
Xiamen University, Xiamen 361005, China
e-mail: lfchen@xmu.edu.cn

H. Gu
Shanghai Institute of Ceramics, Chinese Academy of Sciences,
Shanghai, China

temperature is about 800 °C, silicon carbide fibers with C/Si ≈ 1 are obtainable. Above this temperature, the C/Si ratio will drops below unity, thus resulting in silicon-rich ceramic fibers. Excess silicon is highly detrimental to the high temperature properties of silicon carbide fibers, and hence must be avoided. The C/Si ratio in the final ceramic fibers can be regulated by pyrolysis temperature and hydrogen concentrations in the pyrolysis atmosphere. The as-decarbonized fibers contain a large amount of un-reacted free radicals (pendant chemical bonds). They will react instantly when exposed in air with oxygen, increasing the oxygen content up to $\sim 10\%$ in the ceramic fibers [8]. Therefore, after pyrolysis in hydrogen, the fibers must be immediately heat-treated to over 1000 °C in argon to have the free radicals annihilated. Tazi Hemida et al. [8] and Shimoo et al. [9] have also prepared SiC fibers by pyrolysis in hydrogen. The C/Si ratio ranges from 1.05 to 1.14.

These researchers have attributed the effective removal of carbon by hydrogen to the effects of hydrogen on the different decomposition paths of PCS. In inert atmosphere such as argon, hydrogen (H_2) is the main gas evolved, while in hydrogen-containing atmosphere, methane (CH_4) is the dominant gaseous by-product. However, no convincing explanation has been given on the over removal of carbon in hydrogen-containing atmosphere. To avoid producing silicon-rich silicon carbide fibers, the underlining mechanisms of pyrolysis under hydrogen-containing atmosphere must be understood.

In this work, we have studied the relation between carbon reduction during pyrolysis and the chemical structure of the polymer fibers. A new mechanism for decarbonization has been put forth.

Experimental

Preparation of silicon carbide fibers

Polycarbosilane (PCS) was synthesized following the work of Yajima and his colleagues [1–4]. Its number-average molecular weight is $M_n = 1210$, and its softening point is 200 °C. The precursor was melt-spun under the protection of high purity nitrogen into continuous precursor fibers using a laboratory piston-type melt-spinning machine (MMCH05, Chemat, Northridge, America). The as-spun fibers were irradiated in flowing helium with an electron accelerator (GJ2, Xianfeng Co. Ltd., China). The dose rate was kept at 0.42 kGy s^{-1} when the dosage was below 3 MGy to prevent the fibers from over-heating and fusion; and then the dose rate was increased to 0.84 kGy s^{-1} to the final total dosage, 10 MGy. The as-cured fibers contain 1.88 wt% oxygen because of the slight oxidation during spinning. The average diameter of the as-cured fibers is 28 μm.

The cured fibers were placed into a perforated graphite boat to allow the easy access of reaction gas and the escape of waste gases. The tube-furnace (ID = 30 mm) was first heated to and stabilized at the decarbonization temperature in high-purity nitrogen. The hydrogen flow rate was 200 mL min^{-1}. The sample boat was quickly inserted from <100 °C into the hot-zone for the decarbonization reactions. This heating profile can avoid the uncertainty of decarbonization temperature when a gradual heating rate is used. After the decarbonization, the pyrolysis gas was switched into high purity argon. The fibers were further heated at a heating rate of 5 °C min^{-1} to 1200 or 1600 °C. After holding for 60 min, the fibers were furnace-cooled to room temperature.

Analysis and characterization

Carbon content was determined using Horiba Carbon/Sulfur Analyzer (EMIA-320 V, Horiba Ltd., Japan). Oxygen content was determined using Oxygen/Nitrogen Analyzer (EMGA-620 W, Horiba Ltd., Japan). Silicon content was quantitatively measured by chemical titration method. At least three measurements were made for each point and the average value was used. Phase identification was carried out by X-ray diffraction (XRD) (PANalytical X'Pert PRO diffractometer, PANalytical Corporation, Netherlands) with CuKα radiation. Scanning electron microscopy (XL30, Philips-FEI, Eindhoven, Netherlands) and transmission electron microscopy (JEM-2100 CX, Jeol, Japan) were used for fiber diameter determination and microstructure examination. FTIR spectra were recorded using KBr disc method (Nicolet Avator 360, Thermo, America). Raman spectra were recorded on LabRam I (Dilor Corporation, France). Auger Electron Spectroscopy (AES) analysis was performed on PHI660 (P-E Corporation, America).

Results and discussion

Table 1 shows the chemical compositions of the fibers after pyrolysis in hydrogen and the subsequent heat treatment in argon at 1200 °C. The slight higher oxygen content in the final ceramic fibers than in the as-cured fibers is partially due to the weight loss during pyrolysis, and partially due to the oxygen pick-up from the hydrogen and argon as the fibers are extremely prone to oxidation during pyrolysis even by the tiny amount of oxygen in the atmosphere.

Figure 1 shows that the most significant decarbonization occurs at 600–800 °C. The C/Si ratio of the as-cured PCS precursor fibers is 1.93. After heating at 700 °C for 1 h, it

Table 1 Chemical compositions of the fibers after 1 h decarbonization

Pyrolysis temperature (°C)	Si (wt%)	C (wt%)	O (wt%)	C/Si (atomic)
As-cured fibers	53.64	44.48	1.88	1.93
600	60.51	36.22	3.27	1.40
700	63.48	32.10	4.42	1.18
800	67.93	28.55	3.52	0.98
900	63.98	32.30	3.72	1.18
1000	61.59	34.51	3.90	1.30
1100	60.13	35.99	3.88	1.40

drops to 1.18. At 800 °C for 1 h, the C/Si ratio is reduced to 0.98, indicating that the carbon removal is excessive and the fibers are silicon-rich. Excess silicon is more harmful than excess carbon in terms of high temperature mechanical properties and creep resistance. Therefore, it must be avoided. At even higher heat-treatment temperature, the C/Si ratio increases. When the pyrolysis temperature in hydrogen is 1100 °C, the resultant ceramic fibers contain nearly the same amount of excess carbon as the fibers pyrolyzed in nitrogen (C/Si = 1.40).

When the resident time is prolonged to 4 h at 700 °C, the C/Si ratio is further reduced to 1.08. However, 4 h heat-treatment at 800 °C leads to ceramic fibers with C/Si = 0.90, highly rich in silicon. For decarbonization temperature of ≥900 °C, the curve of 4 h almost completely overlaps with the 1-h curve.

It is clear that silicon carbide fibers with C/Si ≈ 1 can be obtained by optimizing the decarbonization temperature (at 700–800 °C) and holding time. In order to increase the productivity, short reduction time and hence higher temperature is preferred. Therefore, we have examined the change of C/Si with holding time at 800 °C as shown in Fig. 2. Ceramic fibers with C/Si ≈ 1 is obtainable at 0.85 h and the fibers are lustrously black. For holding time of ≥2 h, the C/Si remains essentially constant, and the resultant fibers are reddish-brown because of its richness in silicon.

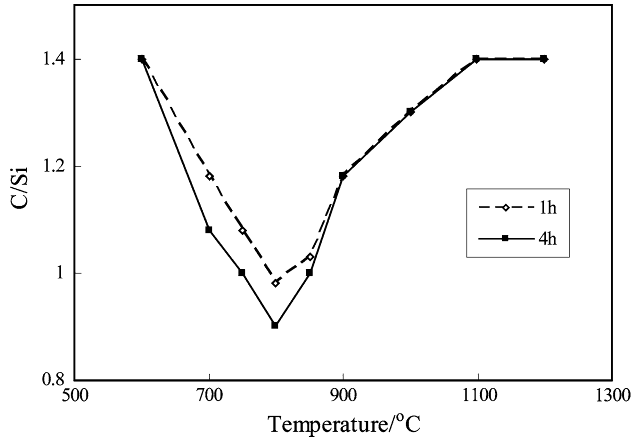

Fig. 1 C/Si ratio as a function of decarbonization temperature

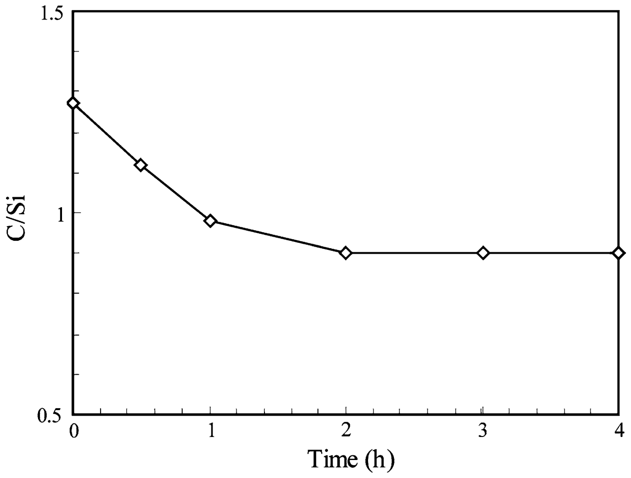

Fig. 2 C/Si ratio as a function of holding time at 800 °C

The above study shows that the decarbonization will not stop at C/Si = 1 and the final ceramic fibers will be silicon-rich with prolonged heating. However, the decarbonization will not go infinitely, rather it will stop when the C/Si ratio has reached to a certain value, C/Si ≈ 0.9 in this work.

Our research and the published work [10, 11] have all shown that the overwhelming organic–inorganic transition of PCS takes place at 550–850 °C in inert atmosphere. On the base of FTIR spectroscopy and gas evolution analysis data in hydrogen and inert atmosphere, Hasegawa et al. [10], Bouillon et al. [11], and Chollon et al. [12], have proposed the pyrolysis mechanisms involving free radical reactions shown in reaction (1) to (8):

$$-\mathrm{Si{-}H} \rightarrow -\mathrm{Si}^{\bullet} + \mathrm{H}^{\bullet} \tag{1}$$

$$-\mathrm{Si{-}CH_3} + \mathrm{H}^{\bullet} \rightarrow -\mathrm{Si{-}CH_2}^{\bullet} + \mathrm{H_2}(\text{Hydrogen removal}) \tag{2}$$

$$-\mathrm{Si{-}H} + -\mathrm{Si{-}CH_3} \rightarrow -\mathrm{Si{-}CH_2{-}Si}- + \mathrm{H_2}(\text{Hydrogen removal}) \tag{3}$$

$$\mathrm{H}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{H_2}(\text{Hydrogen removal}) \tag{4}$$

$$-\mathrm{Si{-}CH_3} \rightarrow -\mathrm{Si}^{\bullet} + \mathrm{CH_3}^{\bullet} \tag{5}$$

$$-\mathrm{Si{-}CH_3} + \mathrm{CH_3^{\bullet}} \rightarrow -\mathrm{Si{-}CH_2}^{\bullet} + \mathrm{CH_4}(\text{Methane removal}) \tag{6}$$

$$-\mathrm{Si{-}CH_3} + -\mathrm{Si{-}CH_3} \rightarrow -\mathrm{Si{-}CH_2{-}Si}- + \mathrm{CH_4}(\text{Methane removal}) \tag{7}$$

$$-\mathrm{CH_3}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{CH_4}(\text{Methane removal}) \tag{8}$$

In inert atmosphere, the relatively weak Si–H and Si–CH_3 bonds break first. Then, the free radicals react with C–H bonds or with each other to form Si–CH_2–Si groups, releasing hydrogen and methane. Below 900 °C, the cleavage of Si–CH_3 is limited, so the major gaseous species evolved is hydrogen. This can effectively explain why the decarbonization is incomplete in inert atmosphere. In hydrogen-containing atmosphere, the hydrogen accelerates the cleavage of Si–CH_3. Therefore, more methyl free radicals (–$CH_3^\bullet$) are generated. They react with hydrogen free radicals ($H^\bullet$) or with C–H bonds to form methane.

One can deduce from Fig. 1 that the reduction of carbon by hydrogen and the ceramicization is competing during pyrolysis. The carbon removal is dominant below 800 °C, while the ceramicization is the major process above 800 °C. Therefore, if the decarbonization temperature is too high, the Si–H, Si–CH_3, and C–H bonds near the fiber surface will cleave into free radicals. However, the free radicals quickly recombine, releasing mainly methane as the exhaust gas. However, the hydrogen from the atmosphere has not got enough time to diffuse into the interior of the fibers, so that thermal decomposition is the major process inside the fiber rather than reduction. Because the initial C/Si ratio of PCS is near to 2, the final ceramic fibers contain a large amount of excess carbon. The excess carbon in the ceramic network is stable, so that it can hardly react with hydrogen. This explains why the decarbonization is more effective below 800 °C. In order to further prove this hypothesis, the as-cured PCS fibers are quickly placed to the furnace hot zone. After soaking for 1 h, they are taken out quickly and cooled to room temperature for analysis. Figure 3 shows the AES profiles for the fibers pyrolyzed at 1000 °C in hydrogen. The overall C/Si ratio of the pyrolyzed fibers was 1.30, although the C/Si ratio is close to unity near the surface. The carbon concentration increases toward the center, forming a uniform concentration gradient and a carbon-rich core. On contrast, the silicon concentration remains essentially unchanged along the radial direction. This experiment shows clearly that the decarbonization of PCS in hydrogen is hydrogen diffusion-controlled process.

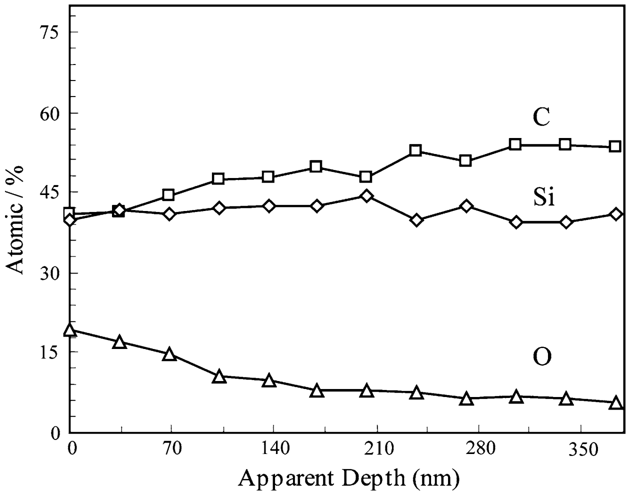

Fig. 3 AES concentration profiles of Si, C and O across the fiber diameter (holding 1 h at 1000 °C)

However, the above free radical reactions (1) to (8) cannot explain the phenomenon of carbon over-removal ($C/Si < 1$) after prolonged heating at 800 °C. Takeda et al. [7] have given a tentative explanation. After the cleavage of Si–H and Si–CH_3 bonds, the more stable Si–CH_2–Si linkages in the backbone chain of PCS start to dissociate into Si–$CH_2^\bullet$ free radicals. The Si–$CH_2^\bullet$ then reacts with $H^\bullet$ to form methane, leading to silicon-rich ceramic fibers. If this is true, the breaking of Si–CH_2 bonds will continue with increasing pyrolysis temperature or the holding time until pure silicon fibers are formed. But, in reality the change of C/Si ratio tends to stop below a certain value, e.g., ~0.9 [7]. Apparently, the above explanation has not disclosed the underlying reasons for the carbon reduction of PCS in hydrogen.

We postulate that the auto-stop of the carbon removal is related to the chemical structure of the as-cured fibers. That is to say, there exist other carbon-containing groups besides Si–H, Si–CH_3, and Si–CH_2. These bonds should be stronger than Si–H and Si–CH_3, but weaker than Si–CH_2. Table 2 shows the possible chemical bonds in PCS together with their bond dissociation energy [13]. Obviously, C–C bonds can meet the above criteria.

In order to detect C–C bonds, the chemical structure of the precursor fibers and as-cured fibers are characterized. Figure 4 shows the FTIR spectra. The strong absorptions at 2100 and 1250 cm^{-1} are assigned to Si–H and Si–CH_3, respectively, while the doublet absorptions at 2950 and 2900 cm^{-1} correspond to C–H stretching of CH_3 and CH_2. Chollon et al. [12] has analyzed electron beam-cured PCS fibers by FTIR and have found new strong absorption at 1450 cm^{-1}. They have attributed it to C–H of CH_2–CH_2 groups. However, in our work, a peak at 1425 cm^{-1} is found for both the precursor fibers and the electron beam-cured fibers. They are assigned to C–H from CH_2–CH_2 (see

Table 2 Dissociation energy of selected chemical bonds

Chemical bonds	Dissociation energy (kJ mol^{-1})	Example
Si–Si	332–336	$(CH_3)_3Si–Si(CH_3)_3$
Si–H	357–380	$(CH_3)_3Si(CH_3)_2Si–H$
C–C	377	$CH_3–CH_3$
Si–C	383–394	$(CH_3)_3Si–CH_3$
C–H	419–425	$CH_3CH_2CH_2CH_2–H$

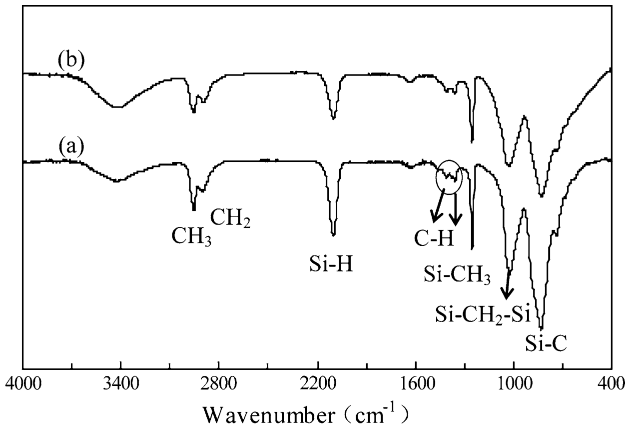

Fig. 4 FTIR spectra of **a** precursor fibers, and **b** electron beam-cured fibers

also the Raman spectra in Fig. 5). The shift of position is believed due to the slightly different chemical structure of the PCS precursors used. The peak areas of Si–H (2100 cm^{-1}, A_{2100}) and Si–CH$_3$ (1250 cm^{-1}, A_{1250}) are normally used to calculate the relative concentration of Si–H bonds. Similarly, the relative concentration of C–H bonds (at 1425 cm^{-1}) is calculated through the peak areas of C–H (A_{1425}) and Si–CH$_3$ (A_{1250}). Table 3 shows the relative concentration of Si–H and C–H (from CH$_2$–CH$_2$ groups) bonds before and after curing. The concentration of Si–H bonds has decreased significantly after curing because of electron beam-induced free radical reaction. However, the relative concentration of C–H bonds remains essentially unchanged, indicating that CH$_2$–CH$_2$ is stable during the irradiation.

It is well-known that C–C bonds are insensitive and difficult to be detected by FTIR. However, they can be analyzed by Raman. Figure 5 is Raman spectra of the precursor and electron beam-cured PCS fibers. Absorption bands at 710 cm^{-1} are observed for both the precursor and irradiation-cured fibers. They are assigned to C–C bonds according to Tazi Hemida et al. [8], further confirming the existence of CH$_2$–CH$_2$ groups in the precursor and cured fibers.

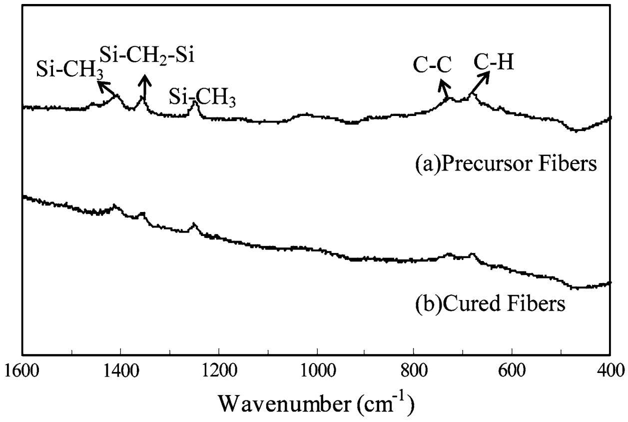

Fig. 5 Raman spectra of **a** precursor fibers, and **b** electron beam-cured fibers

Table 3 Relative concentration of Si–H (2100 cm^{-1}) and C–H (from CH$_2$–CH$_2$ groups, 1425 cm^{-1}) bonds before and after curing

Fibers	Si–H (A_{2100}/A_{1250})	C–H (A_{1425}/A_{1250})
PCS precursor fibers	1.94	0.24
As-cured fibers	1.03	0.25

From the energy point of view, CH$_2$–CH$_2$ groups are most likely to be present in the form of Si–CH$_2$–CH$_2$–Si linkages. Therefore, we believe that the carbon removal during pyrolysis in hydrogen is as follows. At the early stage, reactions (1)–(8) takes place. When these reactions approach to the end, the relatively strong C–C bonds in the Si–CH$_2$–CH$_2$–Si groups are thermally cleaved, leading to the free radical reactions shown in reactions (9)–(12). Finally, methane is released and the C/Si ratio is reduced below unity.

$$-\mathrm{Si}-\mathrm{CH_2}-\mathrm{CH_2}-\mathrm{Si}- \rightarrow -\mathrm{Si}-\mathrm{CH_2}^{\bullet} + {}^{\bullet}\mathrm{CH_2}-\mathrm{Si}- \tag{9}$$

$$-\mathrm{Si}-\mathrm{CH_2}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow -\mathrm{Si}^{\bullet} + \mathrm{CH}_3^{\bullet} \tag{10}$$

$$-\mathrm{Si}^{\bullet} + -\mathrm{Si}-\mathrm{CH_2}^{\bullet} \rightarrow -\mathrm{Si}-\mathrm{CH_2}-\mathrm{Si}- \tag{11}$$

$$\mathrm{CH_3}^{\bullet} + \mathrm{H}^{\bullet} \rightarrow \mathrm{CH_4} \tag{12}$$

According to this mechanism, all the carbon atoms in CH$_2$–CH$_2$ groups will be removed during the final stage of decarbonization. Therefore, one can estimate the concentration of Si–CH$_2$–CH$_2$–Si in the whole PCS structure. First, the backbone of PCS polymer chain is assumed to be

$$-\left[(\mathrm{Si}-\mathrm{CH_2})_m-(\mathrm{Si}-\mathrm{CH_2}-\mathrm{CH_2})_n\right]-$$

At the end of the decarbonization process, the remaining numbers of silicon atoms and carbon atoms are $(m + n)$ and m, respectively. That is to say, the C/Si ratio in the ceramic residue is $m/(m + n)$. In this work, the carbon removal stops at C/Si = 0.9. Therefore, $m/(m + n) = 0.9$, or $n/m = 1/9$. After pyrolysis at 800 °C, the residue should have inter-connected Si–CH$_2$ structure [7]. Because the dissociation energy of Si–C bonds is too high, they will not cleave further. Instead the residue will convert into ceramics by losing hydrogen from CH$_2$ groups. Therefore, in order to prepare SiC fibers with C/Si ratio close to unity, the content of Si–CH$_2$–CH$_2$–Si groups in PCS must be reduced as low as possible.

Figure 6 shows the XRD patterns of the SiC fibers with different C/Si ratios. The fibers are decarbonized in hydrogen and subsequently heat-treated at 1600 °C. All the

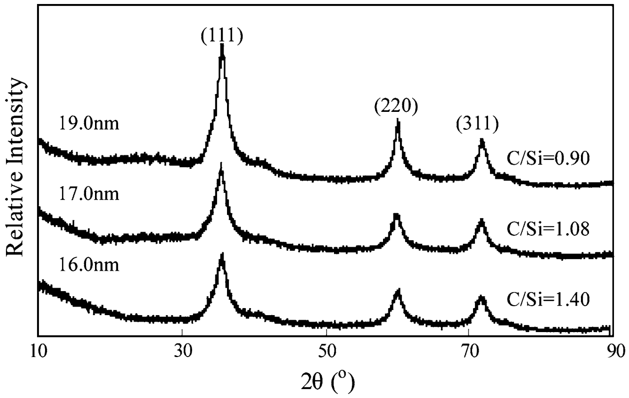

Fig. 6 XRD patterns for of the SiC fibers after decarbonization in hydrogen and the subsequent heat-treatment at 1600 °C

diffraction peaks correspond to β-SiC. The carbon-rich fibers contain smaller grains, because the excess carbon will aggregate at the grain boundary, impeding the grain growth [7, 14]. The silicon-rich fibers have larger grain size than the carbon-rich or C/Si $\approx$ 1, indicating that excess silicon accelerates the grain growth of SiC [7].

Figure 7 shows that the SiC fibers with C/Si $\approx$ 1 and after treatment at 1600 °C are dense. The fracture morphology is typical of brittle materials. It is similar to the glassy fracture surface of Hi-Nicalon® fibers, rather than the granular appearance of Hi-Nicalon Type S® fibers. The TEM photograph (Fig. 8) shows that the SiC grain size is ~10 nm, close to the XRD value calculated from Scherrer's formula. This grain size is similar to Hi-Nicalon® fibers (~5 nm), but much smaller than Hi-Nicalon Type S® fibers (~50 nm) [14]. This is probably due to the fact that the current fibers contain higher percentage of oxygen (~4% against ~0.5% in Hi-Nicalon Type S®). Figure 8 also shows that there exists a small amount of amorphous phase between the small silicon carbide grains, which is attributed to SiC_xO_y phase [7, 14, 15]. It is well known that both excess carbon (such as in Hi-Nicalon® fibers [7, 14]) and oxygen (such as in Nicalon® fibers [14]) can markedly suppress the growth of silicon carbide grains. It has been shown that the oxygen content must be reduced to nearly zero for fibers to be produced with properties approximating to those of stoichiometric silicon carbide. And the existence of excess of SiC_xO_y phase will most probably limit the mechanical properties and encourage creep. Therefore, more stringent processing control is needed to reduce the oxygen content and produce near-stoichiometric silicon carbide fibers similar to Hi-Nicalon Type S®.

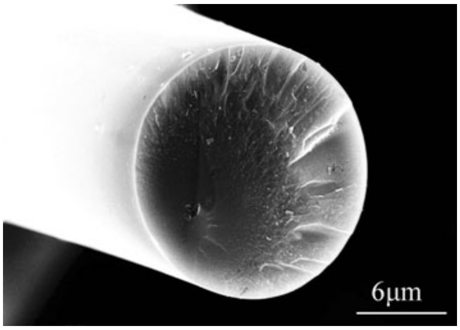

Fig. 7 SEM micrograph of SiC fibers (C/Si = 1.08)

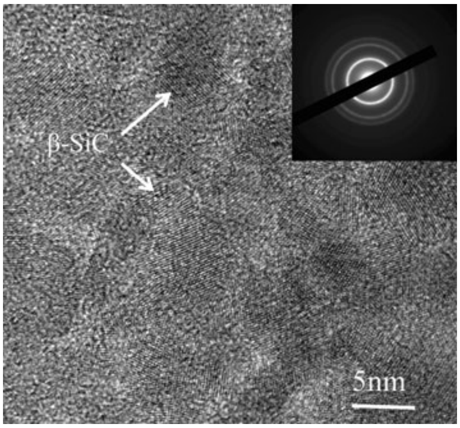

Fig. 8 HRTEM micrograph of SiC fibers (C/Si = 1.08)

Conclusions

When PCS fibers are cured by electron beam irradiation in helium and then pyrolyzed under hydrogen, the excess carbon in PCS can be effectively removed to give silicon carbide fibers with C/Si $\approx$ 1. During pyrolysis, the thermal cleavage of relatively weak Si–H and $Si–CH_3$ bonds takes place first, generating free radicals. The free radicals then react with C–H bonds or with each other to form $Si–CH_2–Si$ groups, releasing hydrogen and methane. As temperature increases, the $Si–CH_2–CH_2–Si$ groups in PCS begin to dissociate and react with hydrogen to form methane, resulting in the further removal of carbon and giving silicon-rich silicon carbide fibers (i.e. C/Si $<$ 1). The concentration of $Si–CH_2–CH_2$ groups has been estimated to be one tenth in the backbone chains of the PCS polymer used in this work. Therefore, it is desired that $Si–CH_2–CH_2$ content should be as low as possible in PCS to produce silicon carbide fibers with C/Si $\approx$ 1.

Acknowledgements The project was supported by National Natural Science Foundation of China (No. 50532010).

References

1. Yajima S, Hayashi J, Omori M et al (1976) Nature 261:683
2. Yajima S, Hayashi J, Omori M (1975) Chem Lett 9:931

3. Yajinla S, Ishishido, Kayano H (1978) Nature 273:525
4. Yajima S, Hasegawa Y, Hayashi J et al (1978) J Mater Sci 13:2569. doi:10.1007/BF02402743
5. Takeda M, Sakamoto J, Imai Y (1994) Ceram Eng Sci Proc 15:133
6. Nakahira A, Hiroshi M, Ichikawa H (2006) J Ceram Soc Jpn 114:455
7. Takeda M, Saeki A, Sakamoto J (2000) J Am Ceram Soc 83:1063
8. Tazi Hemida A, Pailler R, Naslain R (1997) J Mater Sci 32:2359. doi:10.1023/A:1018544805060
9. Shimoo T, Katase Y, Okamura K (2004) J Mater Sci 39:6243. doi:10.1023/B:JMSC.0000043593.01160.da
10. Hasegawa Y, Okamura K (1983) J Mater Sci 18:3633. doi:10.1007/BF00540736
11. Bouillon E, Langlais F, Pailler R et al (1991) J Mater Sci 26:1333. doi:10.1007/BF00544474
12. Chollon G, Czerniak M, Pailler R et al (1997) J Mater Sci 32:893. doi:10.1023/A:1018597432067
13. Luo YR (2003) Handbook of bond dissociation energies in organic compounds. CRC Press, New York
14. Bunsell AR, Piant A (2006) J Mater Sci 41:823. doi:10.1007/s10853-006-6566-z
15. He GW, Shibayama T, Takahashi H (2000) J Mater Sci 35:1153. doi:10.1023/A:1004772000985