Preparation of Si–C–O–N ceramic fibers from polycarbosilane

FAN XIAOLIN*
Institute of Modern Molecular Sciences and Advanced Materials, Gannan Normal College, Jiangxi, 341000, China
E-mail: fanxl2002@yahoo.com.cn

LIU WEI, LU XIUGUO
Department of Chemistry, Hebei University, Hebei, 071002, China

FENG CHUNXIANG, SONG YONGCAI
5th Department, National University of Defense Technology, Changsha, Hunan, 410073, China

Processing of organosilicon polymers to ceramic fibers provide a route to fine diameter, textile grade fibers. Woven and knitted structures are desired to reinforce ceramic matrix or metal matrix composites which can overcome the brittle, catastrophic failure of monolithic ceramics [1].

Nicalon ceramic fibers are converted from polycarbosilane (PCS) through melt spinning, cross-linking, and pyrolysis [2]. The normal structure of PCS is $-(CH_3HSiCH_2-)_x-$ [3], though the actual structure is complexly branched and with CH_3HSiCH_2 and Me_2SiCH_2 functionality contained. The most active bond in the PCS molecule is Si–H due to its low bond strength (315 kJ/mol), the next is Si–C (319.2 kJ/mol). When PCS is heated in an ammonia atmosphere, the molecule may first decompose [4, 5].

$$NH_3 + Si\text{–}H \rightarrow Si\text{–}NH_2 + H_2 \tag{1}$$

$$NH + Si\text{–}H \rightarrow Si\text{–}N = +H_2 \tag{2}$$

If the temperature is high enough to activate the $Si\text{–}CH_3$, the PCS will also decompose in ammonia atmosphere in the following ways.

$$NH_3 + Si\text{–}CH_3 \rightarrow Si\text{–}NH_2 + CH_4 \tag{3}$$

$$NH + Si\text{–}CH_3 \rightarrow Si\text{–}N = +CH_4 \tag{4}$$

Although ammonia is kinetically stable in the gas phase due to its high N–H bond strength (460 kJ/mol), it is thermodynamically unstable above 200 °C. It can be decomposed readily on many surfaces [6, 7]. When the temperature is raised to 500∼800 °C, ammonia may decompose by the following modes.

$$NH_3 \rightarrow {}^{\cdot}H + {}^{\cdot}NH_2 \tag{5}$$

$$NH_3 \rightarrow H_2 + NH \tag{6}$$

When PCS pyrolyzes in ammonia atmosphere, the thermal decomposition of the polymer catalyzes the decomposition of ammonia. The nitridation has been explained as a nucleophilic displacement of carbon and hydrogen by ammonia. Just on this point, the nitridation of PCS is a way to produce Si_3N_4 powders, such as discussed by Burns *et al.* [5].

In this paper, the nitridation of PCS fibers to produce Si–C–O–N fibers is discussed.

To keep the fibril shape unchanged during nitridation, the PCS fibers were first cross-linked in the air at 200 °C for about 4–10 hr. The nitridation of PCS was carried out in a quartz tube furnace at 400–800 °C for 6–12 hr, the gas flow of ammonia is $20\text{–}50 \times 10^{-6}$ m^3/min. After nitridation, the ammoniated fibers were treated at ∼0.5 °C/min to 800 °C, 3.5 °C/min to 1250 °C, then followed by a hold of 1 hr at 1250 °C in nitrogen. The average tensile strength of the fibers was more than 3.2 GPa, some of them reached 4.5 GPa.

The tensile strength of the ceramic fibers was tested at room temperature according to Japanese industrial standard R 7601-1986. Elemental compositions of the ceramic fibers were determined by different methods: carbon and hydrogen by element analyzer model PE-2400II (P. E. Co., USA); nitrogen by N/O determinator (Model TC-436, LECO Co., USA); silicon and oxygen by neutron activation analysis; boron by inductively coupled plasma torch-Auger electron spectroscopy (Model PS-6, Baird Co.). Magnetic resonance spectra of ^{29}Si nuclei were obtained on finely ground powders at 8.45 T, corresponding to a ^{29}Si resonance frequency of 79.4 MHz, using a FT-NMR instrument and magic angle sample spinning.

The process of nitridation was detected by thermogravimetric (TG) analysis. As shown in Fig. 1, the process of nitridation can be discussed in three stages. The first stage is from room temperature to 50 °C. During this stage, the weight of the fibers increased drastically due to two factors. The main reason is the physical absorption in the preceramic fibers because of their high

---

* Author to whom all correspondence should be addressed.

0022-2461 © *2005 Springer Science + Business Media, Inc.*
DOI: 10.1007/s10853-005-4558-z

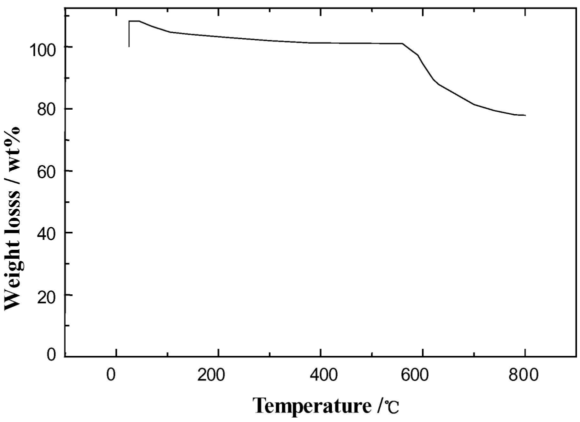

Figure 1 Thermogravimetric curves for ammoniating of PCS fibers with the temperature changed.

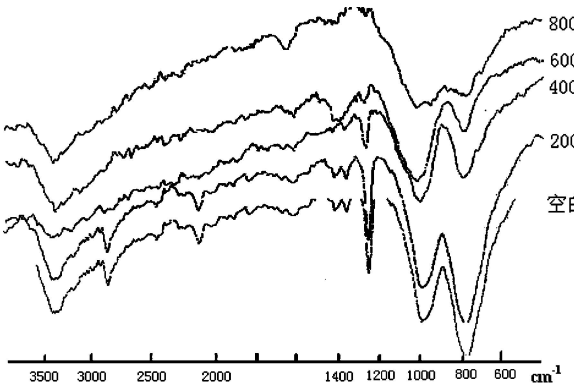

Figure 3 Infrared spectra of PCS fibers ammoniated at different temperatures.

relative surface area. Another reason is the reactions between the reactive functionalities which on the surface of the fibers and NH_3. The weight gain is 8.0 wt% in total. The second stage is 50–560 °C. In this stage, there is a continuous slow weight loss, the fibers lost about 7.5 wt% of their weight because of the desorption of NH_3 which absorbed by physical absorption. In spite of the desorption, by the end of this stage, there is still 0.5 wt% of weight increase in contrast to the original weight. This can be attributed to the irreversible reactions. The third stage is 560–1000 °C. During this stage, the weight loss of the fibers reached 20 wt%. This is because when the temperature reached 400 °C, the decomposition of PCS started. With the temperature elevated, the decomposition of the PCS became more drastic, and the evolution of small molecules such as CH_4 and H_2 increased relatively.

Fig. 2 shows the thermogravimetric curves for ammoniating of PCS at 400 °C. As shown in the graph, first, there was a drastic weight increase when the temperature increased from room temperature to 380 °C, the weight increase was about 7.0 wt% due to the physical absorption; then followed a weight loss and during the temperature increase from 380–400 °C, it lost about 6.7 wt% of its weight; after that, when holding the temperature on 400 °C, the sample kept a continuous stable weight. When the temperature dwell was 4 hr, the weight increase reached 6.5 wt%. This is because of the reactions between Si–H, Si–CH_3 and NH_3.

As shown in Fig. 3, when heated at temperatures below 400 °C, compared to the original PCS, there is no difference in the characteristic absorption in the infrared spectrum except the peak of Si–H at 2100 cm^{-1} became very small according to the integral analysis. When the temperature reached 600 and 800 °C, the case is different, the characteristic absorption at 2100 cm^{-1} disappeared while the peaks at 1250 cm^{-1} became very small, broad N–H stretches at 3400 and 1080 cm^{-1} and Si–N–Si asymmetric stretch at 900 cm^{-1} were observed. The result suggests that at 400 °C, the nucleophilic displacement of Si–H by NH_3 started, when the temperature reached 600 °C, the displacement of Si–CH_3 by NH_3 is begun. The result also suggests that at lower temperature such as 400 °C, using NH_3 crosslinking the PCS fibers is possible, but at higher temperature, the ammoniating of PCS fibers would cause drastic backbone changes in the polymer. The results are partly consistent with those of Burns *et al.* [5]. The case can also be testified by the elemental analysis.

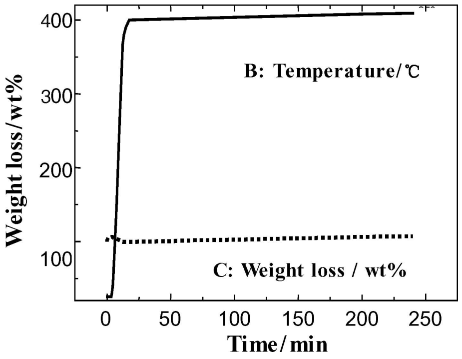

Figure 2 Thermogravimetric curves for ammoniating of PCS fibers at the same temperature. B: TG curve, C: Temperature.

As shown in Table I, at 400 °C, in contrast to the original PCS fibers, the increasing of nitrogen is trivial, and the decreasing of carbon is only 0.3 wt%. But when the temperature reached 600 °C, the loss of carbon is remarkable. Although on the other hand, the content of nitrogen increased and hydrogen decreased, respectively. The decreasing of silicon with the ammoniating temperature is due to the decomposition of PCS and the evolution of small pieces such as Me_3SiH, Me_2SiH_2, $SiMe_4$ and $MeSiH_3$ [4]. As illustrated in the table, in contrast to the SiC fibers originated from the similar PCS fibers, the tensile strength of the fibers obviously increased when ammoniated previously. The results could be due to the crosslinking of many of the Si–H by the NH_3 in the main chain of the molecules.

The nitrogen content in the ammoniated fibers was dependent on the initial temperature of ammoniate, the concentration of ammonia, and the time of ammoniation, the results were shown in Figs 4, 5, and 6. As the temperature of the ammoniate elevated, or the time lasted, or the concentration of ammonia increased, the nitrogen content increased.

As shown in Figs 4 and 5, the nitrogen content increased proportionally with the temperature of ammoniation and the concentration of ammonia. The content of nitrogen at 600 °C was 12.5 wt% in contrast to 360 °C when it was only 2.1 wt%. When the concentration of ammonia in the atmosphere was 10 vol%, the content of nitrogen in the fibers was only 2.0 wt%,

TABLE I Composition of PCS fibers ammoniated at different temperature

Polymer	Ammoniating temperature (°C)	Tensile strength of the ceramic fibers (GPa)	Elemental analysis (wt%) Si	C	O	N	H
PCS fiber		2.0	42.7	35.4	15.5	<0.1	6.3
PCS fiber/NH_3	400	3.2	42.0	35.1	16.3	3.8	4.8
PCS fiber/NH_3	600	3.1	36.5	29.6	18.2	12.5	3.2
PCS fiber/NH_3	800	2.7	35.5	22.5	19.4	18.2	2.1

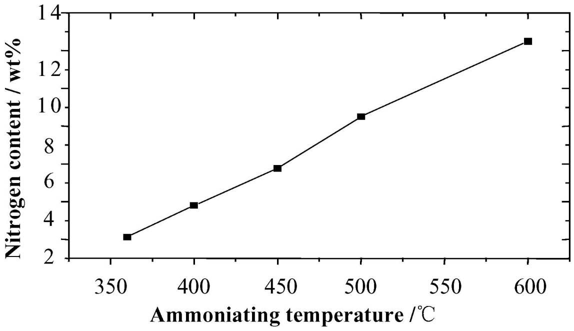

Figure 4 Nitrogen content at different temperatures.

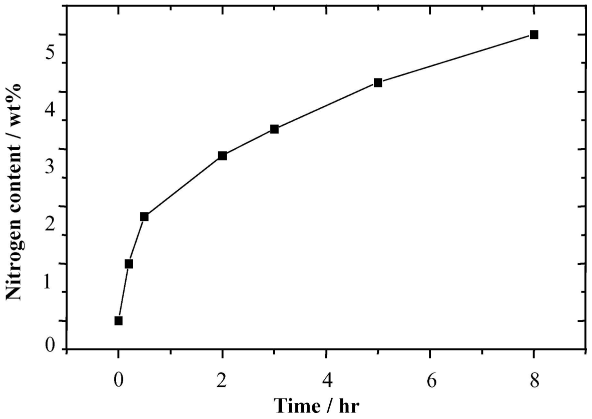

Figure 6 Nitrogen content for different reacting times.

when the content of ammonia increased to 100 vol%, the nitrogen content slowly increased to 3.2 wt%. If the temperature was held at 450 °C, and the concentration of ammonia kept at 40 vol%, but the time of ammoniating varied, the case was different. As Fig. 6 indicated, during the first hour, the content of nitrogen increased drastically with the reacting time, nitrogen in the samples increased from 0.1 wt% to about 2.5 wt%. But in the following hours, the nitrogen increased more slowly than during the first hour, the weight increase was about 2.5 wt% altogether. This is because the ammoniating of PCS fibers first happened to the reactive bonds at the surface or the surface in big holes. At this stage, the speed is only controlled by the reaction itself. When ammonia molecules penetrated into the inner parts of the fibers, the inner ammoniation began. At this stage, the speed of ammoniating was not only controlled by the reaction itself, but also controlled by the penetration of the NH_3.

The elemental analysis is also consistent with both the IR and ^{29}Si NMR studies. As shown in Fig. 3, the nitrogen content variation with the temperature of ammoniating is consistent with the infrared spectra. IR analysis for the fibers ammoniated at 400 °C shows that only the Si–H absorption at 2100 cm^{-1} minimized in contrast to that of the original fibers, the characteristic absorption of N–H stretches at 3400 and 1080 cm^{-1} and Si–N–Si asymmetric stretch at 900 cm^{-1} were not obviously observed. However, by 600 °C, broad N–H stretches at 3400 and 1080 cm^{-1} and Si–N–Si asymmetric stretch at 900 cm^{-1} were observed in all the samples. In addition, the Si–CH_3 stretches at 1250 cm^{-1} disappeared. The result suggests the loss of the Si–H and Si–C polymer backbone for PCS, respectively, and the formation of a Si–N type residue.

Solid-state ^{29}Si NMR in Fig. 7 also suggests the formation of a Si–N bond for the ammoniated fibers pyrolysized at 1250 °C. Ceramic fibers from the ammoniated PCS fibers which were pyrolysed in ammonia at 400 °C for 8 hr, peaks at −44.4 ppm (SiN_4), −51.5 ppm (β-Si_3N_4) and −64 ppm (Si_2N_2O) were observed in the ^{29}Si NMR spectrum. They correspond to silicon bonded to nitrogen. Thus, the conversion involves: first, the removal of hydrogen, then at high temperature (>600 °C), the removal of carbon. Presumably, the process can be explained as a nucleophilic displacement of hydrogen and carbon by the attack of NH_2 radicals.

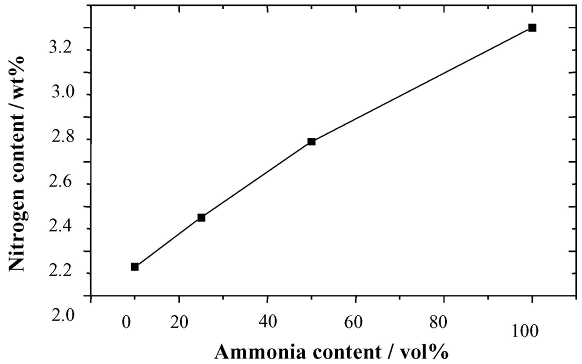

Figure 5 Nitrogen content for different concentrations of ammonia.

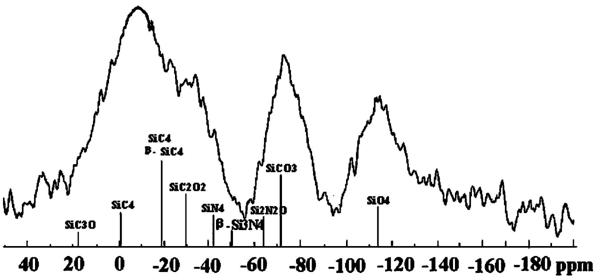

Figure 7 ^{29}Si MAS-NMR spectrum of powdered Si–C–O–N ceramic fiber.

In summary, Si–C–O–N ceramic fibers were obtained by ammoniation of PCS fibers, and the ammoniate procession could be discussed in three stages: the first stage is from room temperature to 50 °C; the second stage is 50–560 °C; the third stage is 560–1000 °C. The process can be explained as a nucleophilic displacement of hydrogen and carbon by the attack of NH_2 radicals. The mechanism of pyrolysis could be detect by IR, ^{29}Si MAS-NMR and elemental analysis. The content of nitrogen in the samples varied with the ammoniating time, the concentration of ammonia and the ammoniating temperature. The tensile strength of the ceramic fibers obtained by this method increased obviously, the average tensile strength of the fibers prepared by this method reached 3.2 GPa.

References

1. T. MAH, M. G. MENDIRATTA, A. P. KATZ and K. S. MAZDIYASNI, *Am. Ceram. Soc. Bull.* **66** (1987) 304–308, 317.
2. N. R. LANGLEY, G. E. LEGROW and J. LIPOWITZ, in "Fiber reinforced ceramic composites", Chap. 3, edited by K. S. Mazdiyasni (Noyes, Park Ridge, NJ, 1990) p. 63.
3. S. YAJIMA, *Am. Ceram. Soc. Bull.* **62** (1983) 893.
4. R. J. P. CORRIU, D. LECLERCQ, P. H. MUTIN and A. VIOUX, *Chem. Mater.* **4** (1992) 711.
5. G. T. BUMS and G. CHANDRA, *Commun. Am. Ceram. Soc.* **72**(2) (1989) 333.
6. C. H. BAMFORD and C. F. H. TIPPER, "Chemical Kinetics" (Elsevier, NY, 1972) Vol. 4, p. 12.
7. C. H. HINSHELWOOD and R. E. BURK, *J. Chem. Soc.* **127** (1925) 1105.

Received 15 April 2004
and accepted 14 April 2005