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Preparation of silicon oxycarbide glass fibers from organically modified silicates

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Silicon oxycarbide glass fibers have been successfully drawn from organically modified silicates (ORMOSILs) by the sol-gel method. The gel fibers were drawn from a precursor composed of tetraethyl orthosilicate (TEOS) and polydimethyl siloxane (PDMS) with different weight fraction. The organics in the fiber underwent decomposition to at temperatures higher than 300°C. The existence of oxycarbide phases were detected using infrared spectroscopy and solid state ^{29}Si NMR and was found in the fibers with heating temperatures higher than 700°C in nitrogen atmosphere. X-ray powder diffraction patterns showed that the fibers were still amorphous even after heat treatment at 1000°C for one hour. © *2000 Kluwer Academic Publishers*

1. Introduction

Silicon oxycarbide glasses are black glasses which have been shown to possess interesting properties differing from pure fused silica, including increases mechanical strength, electrical conductivity, and devitrification resistance [1–5]. In addition, oxidation resistance of the black glasses was also reported [6]. For making black glasses, methods such as conventional melting techniques with silicon carbide as the source of carbon [1, 4] and carbonization of organic substances impregnating micropores of porous SiO_2 glass [3] have been utilized. However, there are difficulties in these methods for making a homogeneous Si–C–O network structure and making more complex shapes such as fibers and thin films. Commercial Si–C–O fibers derived from polycarbosilane polymer have been used for the precursor of silicon carbide fibers [6–8]. However, these fibers are poorly resistant to oxidation at elevated temperatures.

Recently, the sol-gel method has become a new method to prepare black glasses [9–13]. The general character of high reactivity resulting from the sol-gel routes permits low-temperature processing and allows the incorporation of suitable polymeric/oligomeric components into the sol-gel network, if such polymers or oligomers have appropriate functional groups. In a more practical sense, various products such as fibers, films, and composites can be processed by this method. Therefore, it is possible to prepare oxycarbide fibers for the application of fiber reinforced composites.

A number of organic-inorganic hybrid materials have been successfully prepared by the sol-gel method within past ten years [14–17]. These materials are called organically modified silicates (ORMOSILs) or organically modified ceramics (Ormocers of Ceramers) and have also been used as precursors for the black glass [12, 13]. However, there are no reports on the preparation of fibers made from ORMOSILs. In the present study, ORMOSIL fibers were prepared by the sol-gel method and used as a starting material for fabricating silicon oxycarbide glass fibers.

2. Experimental procedure

The precursors of ORMOSILs were prepared using TEOS and PDMS as the inorganic and organic components, respectively. First, a total 60 g weight of TEOS—PDMS was mixed with Tetrahydrofuran (THF, 10 ml) and isopropanol (20 ml) solution in a triple neck flask using a Teflon coated magnetic stirrer. Next, a completely mixed isopropanol (10 ml)-HCl-water solution with the molar ratio of $HCl/TEOS = 0.05$ and $H_2O/TEOS = 3$ was added to the flask. The combined solution was vigorously stirred at 80°C for 2 hours. After cooling to room temperature, the solution was kept in a refrigerator at 5°C for 24 hours and then brought to room temperature as fiber precursors.

The gel fibers were obtained by dipping a glass stick and pulling it up by hand when the precursor had the capability of fiberization. The pulling rate as estimated is about 2–5 cm/sec. These gel fibers were put in a quartz crucible and dried at 70°C in an oven in air for 24 hours and then heated in a fused silica tube furnace to various temperatures (ranging from 300 to 1000°C) for one hour under flowing nitrogen gas at an average heating rate of about 5°C/min.

Thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) (Perkin-Elmer model 1700) were used to evaluate the thermal reactions with the conversion of the gel to black glass. The morphologies of the drawn fibers were examined by scanning electron microscopy (SEM). Powder x-ray diffraction was performed on a diffractometer using Cu K_α radiation. IR spectra of the fibers in the range from

2000 to 200 cm^{-1} were conducted by a spectrometer (Perkin-Elmer model 1330) with KBr disc method. ^{29}Si CPMAS NMR spectra of the fibers were obtained using a spectrometer (MSL 300 Bruker). The spectra were recorded at 59.6 MHz, with relaxation delay of ~10 seconds, polarization time of ~2800 microseconds and 90° pulse for the proton was 7.1 microseconds.

3. Results

The gel fibers, which have been drawn by hand, have the length ranging from 2 to 10 cm as shown in Fig. 1a. Fig.1b shows the SEM photograph of the gel fiber (PDMS/TEOS = 20/80) dried at 100°C. The gel fibers are transparent and uniform with a circular cross section. The diameter of the gel fibers ranged from 50 to 120 μm. The variation in the diameter of the fibers is dependent on the viscosity of the precursor and the pulling rate. It was observed that fibers began to become slightly black at about 300°C.

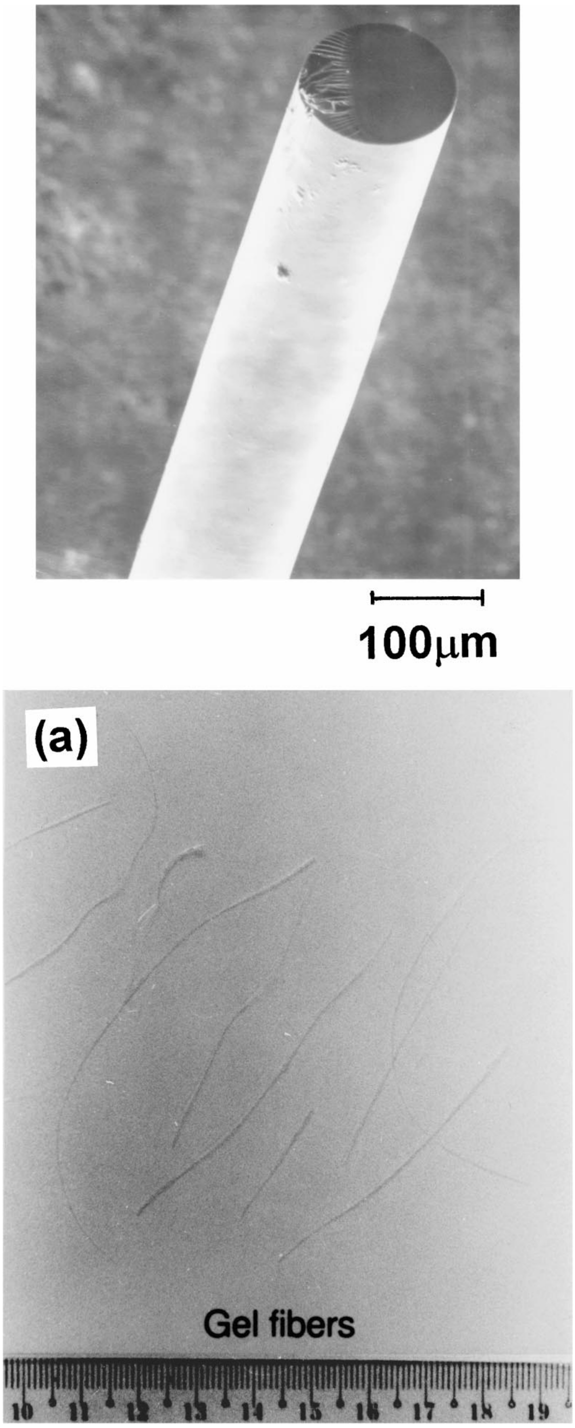

Figure 1 (a) The gel fibers prepared from ORMOSILs by hand drawing; (b) An Ormosil gel fiber heated at 100°C in air for one hour.

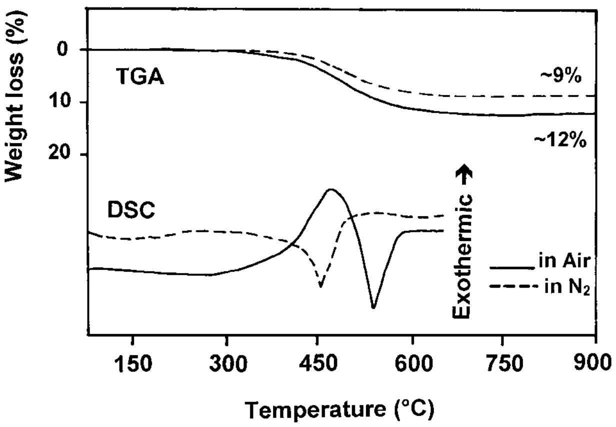

Figure 2 DSC and TGA thermograms of the gel fibers with a heating rate of 5°C/min.

DSC and TGA thermograms of the drawn fibers (PDMS/TEOS = 30/70) are shown in Fig. 2. The TGA curves show about 9% weight loss in nitrogen and 12% weight losses in air between 200 to 600°C for the fiber with PDMS/TEOS = 20/80. These weight losses are assigned to the loss of absorbed water and to the decomposition of Si–CH_3. A broad exothermic peak was found at 350–500°C in the sample heated in air atmosphere and was ascribed to the oxidation reaction of PDMS. It was found that an endothermic reaction peak in the DSC thermograms at about 515°C in air and about 460°C in nitrogen and was attributed to the decomposition of CH_3 group. This absorption band of CH_3 as shown in the IR spectra (Fig. 5) vanished when the fibers were heated at 700°C.

SEM photograph of the black fibers heated at 1000°C for one hour in nitrogen is shown in Fig. 3. Nonuniform shrinkage of the fiber with higher PDMS weight fraction in the heating process results in an irregular shape.

X-ray diffractograms for powdered fibers with different heat treatment are shown in Fig. 4. The samples are still amorphous even after heat-treated at 1000°C for one hour. It is also found that the broad bands of the diffractograms shifted to lower angle when samples were heat treated at higher temperature, i.e., from $2\theta = 24°$ (gel) to $2\theta = 22°$ (heated at 1000°C for one hour). Though the decrease in the diffracted angles has been explained by the increase of the connectivity of the structural network [18], the evolution of the glassy structure should be further examined by other techniques.

The infrared spectra of fibers heated at different temperatures for one hour are given in Fig. 5. The absorptions at 1260, 860, and 805 cm^{-1} in the spectra are the characteristics of the S–C stretching vibration from CH_3 group of PDMS, and the absorption bands at 1110–1080 and 450 cm^{-1} are attributed to vibration of the Si–O bond. Appearance of the absorption band at 950 cm^{-1}, which was believed to be due to Si–OH

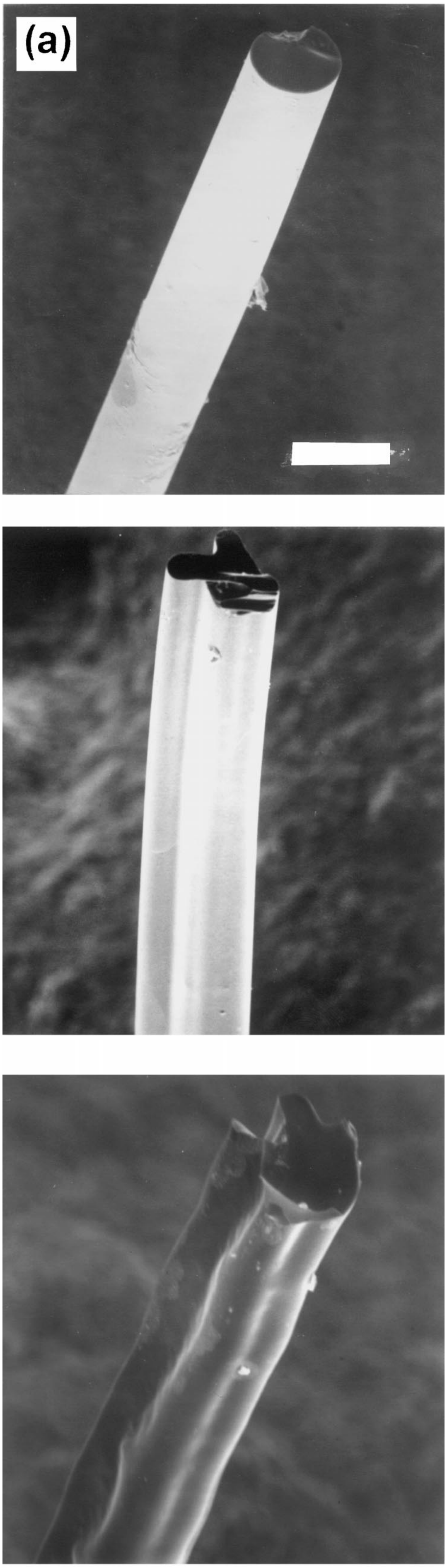

Figure 3 SEM photographs of the silicon oxycarbide fibers with PDMS/TEOS = (a) 10/90, (b) 20/80, (c) 30/70, heat treated at 1000°C in nitrogen for one hour. The white bar represents 100 μm.

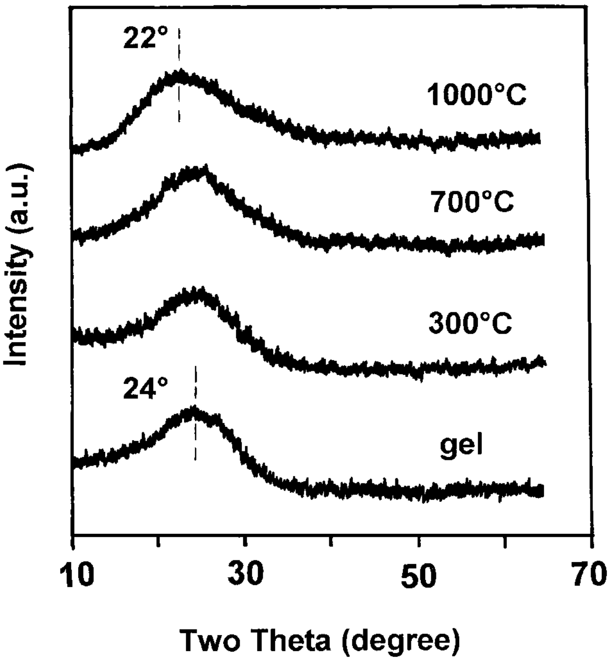

Figure 4 X-ray powder diffraction pattern of the fibers heated at different temperatures for one hour.

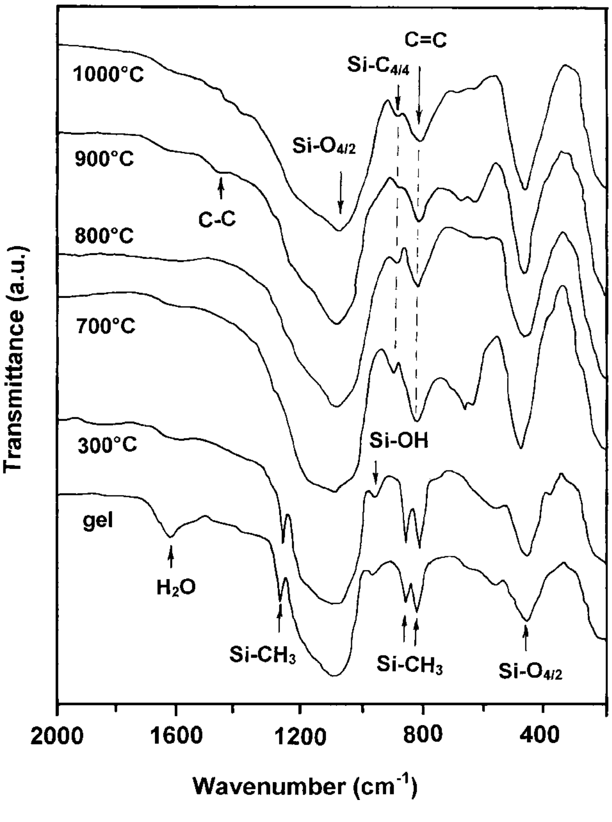

Figure 5 IR spectra of the fibers heated at different temperatures for one hour.

bond, indicated that polycondensation reaction was not completed.

Upon heating to 500°C, CH_3 of PDMS dissociates and the absorption bands of Si–$C_{4/4}$ bonds at 920 and 870 cm^{-1} were observed. The absorption peak at about 670 cm^{-1}, which may be due to the stretching vibration of C–H linkage, became strong. Further heating the fibers at temperatures higher than 700°C, the IR spectra show the same bands attributable to siloxane bonds

(Si–O–Si) and Si–C–Si bonds at (1080, 807, 480) cm^{-1} [19] and (925, 830) cm^{-1} [20], respectively. The band at 1525 cm^{-1} can be attributed to the C–O linkage as reported [21]. Therefore, the IR spectra revealed the existence of the Si–C, Si–O, and C–O bonds in the black glass fibers with $Si_xC_yO_z$ products that has been evidenced by Lipowitz *et al.* [22] and observed in different organic systems [23, 24].

In looking at the ^{29}Si NMR results shown in Fig. 6, the shift at −19.6 ppm is due to the PDMS unit in the PDMS-TEOS copolymer and will hereafter be referred to as a DQ$_j$-unit [9]. The peak at −105 ppm arises from a so-called Q^3 unit (HO–Si–$O_{3/2}$) [9, 25] of which Si–OH bond was also found in the IR absorption as mentioned previously. The peak at −110 ppm is attributed to Q^4 unit (Si–$O_{4/4}$) [9, 26]. At 500°C, the intensity of Q^3 peak decreases to just a shoulder and a new peak at −68 ppm emerges as a T-unit (Si–CO_3) [25, 27]. The relative intensity of the DQ$_j$, T, and Q^4 peaks increased without Q^3 peak when the heating temperature increased. Upon heating to 800°C, an additional small peak S at −21 ppm that is supposed from the bond of Si–C_2O_2 was observed [26, 25]. It was also found that the position of DQ$_j$, S, and T peaks also changed, shifting upfield to more negative values as the temperature increased. This trend indicates that the connectivity of the network is increasing as also observed in the x-ray diffraction analysis. The extremely large shift on the order of −16 to −27 ppm for the T and DQ$_j$ peaks, respectively, indicates that the carbons are crosslinking. The broad peaks in the NMR spectra also provide strong evidence for a glassy phase in the resultant fibers with nearest neighbor bonding about silicon in a random distribution.

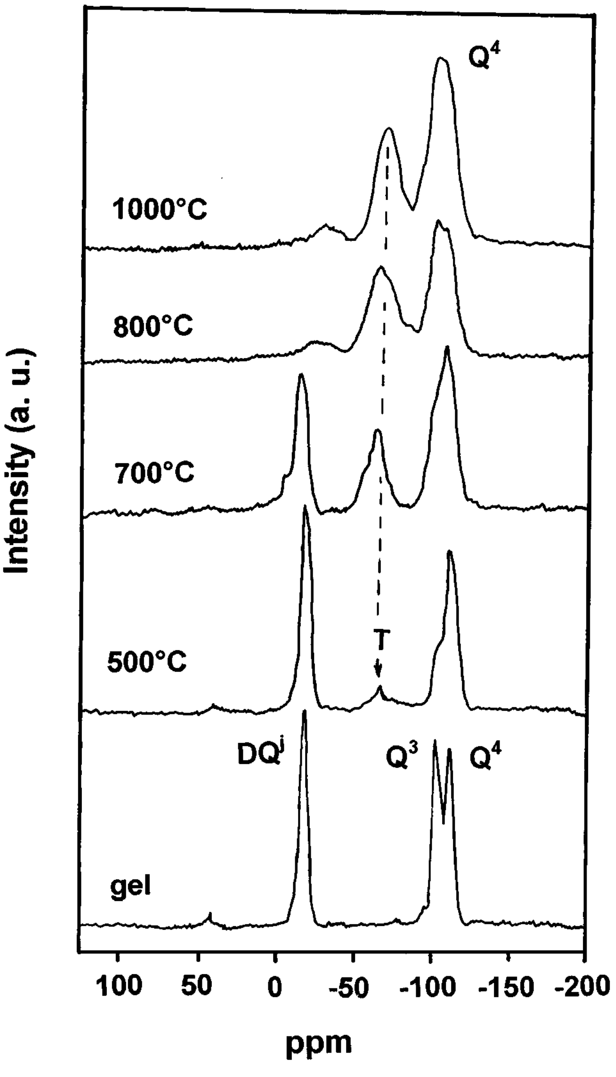

Figure 6 Solid state ^{29}Si NMR spectra of the fibers heated at different temperatures for one hour.

Solid-state ^{29}Si NMR and infrared spectroscopy provide strong evidence for the oxycarbide phases in the fibers. There are three possible tetrahedra for carbon and oxygen groups bonded to silicon which gives three major ^{29}Si signals observed in the NMR spectra (SiO_4, $SiCO_3$, SiC_2O_2). It is suggested that the formation of Si–C–O bond is from the pyrolysis of organic groups in PDMS. The phase evolution based on the ^{29}Si NMR and IR spectra analyses can be elucidated simply as following two steps: (1) Polycondensation between PDMS and TEOS, and (2) Pyrolysis of PDMS and formation of S–C–O bonds. These amorphous covalent structures appear to be the continuous phase in the fibers.

The bulk density and apparent density of Ormosil gel fibers, measured using a Micrometrics Autopcynometer 1320 with helium, are 1.21 and 1.47 g/cm^3, respectively. The variations in density of fibers with different heating temperatures are shown in Fig. 7. The increase in the density with increasing heating temperature as suggested be ascribed to the increase of connectivity of the structural network that was observed in the IR and NMR analysis. A slight decrease in the density with the heating temperature from 300 to 600°C is due to the dissociation of organic groups and evidenced from the endothermic peak of DSC analysis. When the heating temperature was higher than 600°C, the rapid increase of the density of the fibers is attributed to the densification process. The bulk density and apparent density of the fibers heated at 1000°C are 1.54 and 1.80 g/cm^3, respectively. The average tensile strength of the Ormosil gel fibers and the oxycarbide glass fibers heated at 1000°C are about 32 and 68 MPa, respectively.

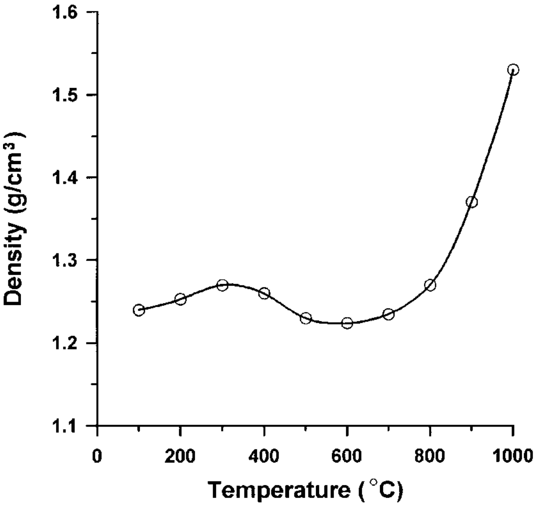

Figure 7 Bulk density of the fibers with different heating temperatures for one hour.

4. Conclusion

Silicon oxycarbide glass fibers have been successfully drawn from an organically modified silicate by sol-gel method. Tetraethyl orthosilicate (TEOS) and Polydimethyl siloxane (PDMS) were used as the inorganic and organic parts, respectively. The existence of Si–C, C–O, and Si–O bonds were revealed using solid state ^{29}Si NMR and infrared spectroscopy. The fibers started to become black from transparency at 300°C due to the dissociation of organic groups. The fibers were found to be amorphous, which is examined by X-ray diffraction analysis even after heating at 1000°C for one hour in nitrogen atmosphere.

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