Structure of nanofibers derived from polycarbosilane using the polymer blend technique

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Polycarbosilane particles were dispersed in a novolac-phenolic resin matrix, and the resulting polymer blend was melt-spun, stabilized and heat-treated at 1000 °C or 1200 °C for 1 h in an inert atmosphere. The heat-treated blend fibers were oxidized in nitric acid solution to remove the carbon matrix and the nanofibers thus released were collected by filtration. The nanofibers obtained from the 1000 °C-blend fibers were oxidized more severely by nitric acid, resulting in a rougher nanofiber surface compared with that of nanofibers from the 1200 °C-blend fibers. The former nanofibers also showed a larger specific surface area (288 m²/g) than did the latter (44 m²/g). Analysis of a filament from the 1200 °C-nanofibers showed carbon present at about 30 atom %, whereas just a few atom % of carbon was found in the 1000 °C-nanofiber. It was concluded that more intact nanofibers with stronger oxidation resistance were derived from the polymer blend fibers heated at a higher temperature.

KEYWORDS : Silicon carbide, Nanofiber, Polymer blend, Spinning

1. Introduction

Nanocomposites incorporating carbon nanotubes (CNTs) and carbon nanofibers (CNFs) as fillers have attracted considerable interest in recent years¹⁾⁻³⁾. However, such carbon materials cannot be used for composites consisting of metal or ceramic matrices because of their poor oxidation resistance. For these composites, silicon carbide can be successfully used instead⁴⁾. As for silicon carbide nanofibers, only whiskers are commercially available at present^{5), 6)}. These whiskers, however, have some practical problems associated with them : a small aspect ratio leading to low reinforcement ; high price reflecting difficulty of mass production ; and so on. This is the motivation behind the authors' development of a new method for preparing nanofibers from polycarbosilane (PCS) materials - a precursor of silicon carbide - by using the polymer blend technique⁷⁾⁻⁹⁾.

In this method, PCS is initially dispersed in novolac-phenolic resin (PF) and the resulting polymer blend is melt-spun. The blend fibers are stabilized, followed by heating to around 1000 °C in an inert atmosphere to carbonize the PF matrix and to transform PCS into an inorganic silicon carbide-based material. Finally, the fibers are oxidized in nitric acid to remove the carbon matrix, and the nanofibers thus released are recovered by filtration. The resulting nanofibers are several hundreds of nm in diameter and are long,

possibly longer than 100 μm.

The authors' focus in this paper is oxidation of the nanofibers during the removal of matrix carbon by nitric acid. In particular, it was thought that nanofibers obtained from blend fibers heated at moderate temperatures were incompletely converted to inorganic material, and as a result, were subject to more severe oxidation. A commercial silicon carbide-based fiber, Nicalon, also shows inferior mechanical properties at high temperature with increasing oxygen content¹⁰⁾. In the present work, the nanofibers were obtained from PCS/PF blend fibers heated at 1000 °C or 1200 °C, and their structures were examined by use of microscopic observations and other techniques.

2. Experimental

2.1 Materials

Polycarbosilane ($[-SiH(CH_3)CH_2-]_n$, PCS type L, softening point 80 °C) was purchased from Nippon Carbon Co. Ltd. Novolac-phenol formaldehyde resin (PF, softening point 100 °C) was kindly supplied by Gun-ei Chemical Co. Ltd.

2.2 Preparation of nanofibers

PCS and PF were completely dissolved in tetrahydrofuran, and the solvent was removed using a rotary evaporator to obtain a polymer blend, in which fine PCS particles were dispersed in a PF matrix. The blend was dried at 60 °C under reduced pressure overnight and then continuously melt-spun at 100 ~ 110 °C under an argon atmosphere

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using a conventional melt-spinning apparatus.

The polymer blend fibers were soaked for 16 h in an acid solution containing hydrochloric acid and formaldehyde as the main components, heated to 110 °C at 0.2 °C/min and held for 16 h to cure the PF matrix. The cured fibers were heated at 1000 °C or 1200 °C under a nitrogen atmosphere. The heating rate and holding time were 100 °C/h and 1 h, respectively. The resulting fibers were oxidized in 60 % nitric acid at 180 °C for 10 h with gentle stirring and finally filtered using a 5 µm membrane filter.

2.3 Measurements

The nanofibers were studied using a scanning electron microscope (SEM : JEOL JSM 5300), a field emission scanning electron microscope (FE-SEM : JEOL JSM 6700) and a transmission electron microscope (TEM : JEOL JEM-2010). An X-ray diffractometer (Rigaku RINT2000/PC) with CuK α -radiation was used to examine the crystalline structure of the nanofibers. An automatic adsorption/desorption apparatus (Nippon Bell, Belsorp 28SA) was used to analyze the porous structure of the nanofibers using nitrogen gas as the absorbent at -196 °C (77 K). The nanofibers were pre-treated at 200 °C for 2 h before the measurement. The elemental composition of a monofilament of the nanofiber was measured by an X-ray photoelectron spectrometer (XPS : Thermo Electron Theta Probe) using AlK α radiation by Sumika Chemical Analysis Service Co. A filament was etched with Ar⁺ ions for up to 2500 sec, with the etch rate corresponding to 0.18 nm/sec for SiO₂ film.

3. Results and discussion

Fig.1 shows SEM photographs of the nanofibers obtained from blend fibers heated at 1000 °C and 1200 °C, respectively referred to as 1000 °C- and 1200 °C-nanofibers. The average diameter of the nanofibers was below 1 µm, although some scatter was seen in the diameters of both types of nanofibers. The 1000 °C-nanofibers (**Fig.1a**) were shorter than the 1200 °C-nanofibers (**Fig.1b**), because the former seemed to be fragile and were broken during the stirring in nitric acid. It should be noted that the nanofibers, particularly the 1200 °C-nanofibers, were straight and very long.

Fig.2 shows FE-SEM photographs of the 1000 °C- and 1200 °C-nanofibers. There was some variability in the appearance of these nanofibers, but on the whole, the 1200 °C-nanofiber showed a

smoother surface than did the 1000 °C-nanofibers. **Fig.2a**) shows severe damage on a 1000 °C-nanofiber. A very fine unevenness (pebble-like structure of ca. 10 nm) was seen in both types of nanofiber.

Certain features of the nanofibers stood out at high magnification. **Figs.3** and **4** show TEM photographs of the 1000 °C- and 1200 °C-nanofibers. The structures depicted were generally seen in both types of nanofiber. As evident from **Fig.3a**) and b), the surface of the 1000 °C-nanofiber was very rough, possibly because of severe oxidation by nitric acid¹¹⁾. Etched spots were occasionally observed, as illustrated in **Fig.3c**). Such etched spots were also observed in the 1200 °C-nanofibers (**Fig.4a**), but the surface of the 1200 °C-nanofiber was far smoother (**Fig.4b**), compared with that of the 1000 °C-nanofiber.

As mentioned above, a major concern of the authors was whether a large amount of oxygen was being introduced into the nanofibers dur-

Fig.2 FE-SEM photographs of nanofibers obtained from a) 1000 °C-blend fibers and b) 1200 °C-blend fibers.

Fig.3 TEM photographs of nanofibers obtained from 1000 °C-blend fibers.

Fig.4 TEM photographs of nanofibers obtained from 1200 °C-blend fibers.

Fig.1 SEM photographs of nanofibers obtained from a) 1000 °C-blend fibers and b) 1200 °C-blend fibers.

Fig. 5 Changes in elemental composition of a monofilament obtained from 1000 °C-nanofibers as a function of etch time.

*The etch rate was 0.18 nm/sec for SiO₂ film.

Fig. 6 Changes in elemental composition of a nanofilament obtained from 1200 °C-nanofibers as a function of etch time.

*The etch rate was 0.18 nm/sec for SiO₂ film.

ing the nitric acid oxidation process. **Figs. 5** and **6** show changes in the elemental composition of filaments of 1000 °C- and 1200 °C-nanofibers as a function of increasing etch time (i.e., distance from the surface). An etch time of 2500 sec corresponded to a depth of 450 nm for SiO₂ film. The 1000 °C-filament contained a large amount of oxygen and just a slight amount of carbon as one would expect based on the rough surface seen in the TEM photograph (**Fig. 3**). The elemental composition remained unchanged in the filament interior. **Fig. 6** suggests that filaments of 1200 °C-nanofibers were more oxidation resistant than the 1000 °C-filaments. The atom % oxygen decreased gradually from the filament surface to the interior and reached ca. 30 atom % at 2500 sec. The carbon and silicon contents showed opposite behaviors, and the filament interior was found to contain a roughly constant C : Si : O atomic ratio of 1 : 1 : 1.

Fig. 7 shows XRD profiles of the nanofibers. Both nanofiber types showed very broad bands. The 1000 °C-nanofibers were expected to consist primarily of amorphous silicon oxide, from **Fig. 5**. It was not easy to deduce the structure of the 1200 °C-nanofibers, but the elemental composition shown in **Fig. 6** corresponded to an

Fig. 7 XRD profiles of nanofibers obtained from 1000 °C-blend fibers and 1200 °C-blend fibers.

Fig. 8 Adsorption/desorption isotherms of nanofibers obtained from 1000 °C-blend fibers and 1200 °C-blend fibers.

amorphous silicon oxycarbide.

As stated above, the nanofibers were oxidized severely by nitric acid. It was quite reasonable to assume that pores were generated by this oxidation process. **Fig. 8** shows the adsorption/desorption isotherms for both types of nanofiber. Several important points were deduced from the isotherms. Micropores were formed in the 1000 °C-nanofibers more abundantly than in the 1200 °C-nanofibers. Both kinds of nanofibers showed an increase in the adsorbed amount of nitrogen at high P/P_o , suggesting the presence of macropores. Minor hysteresis was observed between adsorption and desorption isotherms for these nanofibers. It was also surmised that a small amount of mesopores was formed. The specific surface areas (SSA), which are substantially dependent on micropore volume, were 288 m²/g and 44 m²/g for the 1000 °C- and 1200 °C-nanofibers, respectively.

The chemical compositions of the two different monofilaments were shown in **Figs. 5** and **6**. Here the following point should be noted. As may be easily supposed, nanofibers in the vicinity of the blend fiber surface were likely released before those in the interior. The former nanofibers would therefore have been oxidized for longer than the latter. Thus, the samples examined doubtless included nanofibers oxidized to varying degrees. It is difficult to gauge from

Figs.5 and **6** how severely the monofilaments were oxidized. Nevertheless, the significance of the temperature at which the blend fibers were heated was clear, as discussed below. The nanofibers will be evaluated from two points of view, namely with respect to defects and elemental composition. Defects will be discussed initially.

There were two kinds of defects in these nanofibers. One was the surface roughness of the nanofibers, easily recognized in the FE-SEM and the TEM photographs. It was clear from the photographs that nanofibers obtained from the blend fiber heated at 1200 °C had fewer defects and a smoother surface. Another defect was nitric acid-induced pores, which could be evaluated based on the SSA. The nanofibers prepared from blend fibers heated at 1200 °C also had the smaller SSA. However, it is known that the high mechanical strength of commercially available PCS-derived Nicalon fiber is drastically reduced upon crystallization induced by heating to temperatures possibly higher than around 1350 °C¹²⁾. This behavior would also be expected of the nanofibers in this study. It could be concluded, therefore, that in order to prepare high quality nanofibers by the present method, the blend fiber needed to be heated at the highest temperature possible without inducing crystallization, because PCS is transformed more completely to an inorganic material at higher temperature.

The next factor is the elemental composition of the nanofibers. The compounds formed in PCS upon heating have been discussed in detail on the basis of XPS data¹³⁾. As stated above, however, the nanofibers prepared in the present work were individually subjected to varying degrees of oxidation, and it was impossible to know how severely the monofilaments shown in **Figs.5** and **6** were oxidized. Consequently, only differences in elemental composition between the 1000 °C- and the 1200 °C-nanofibers will be briefly discussed.

The 1000 °C-monofilament shown in **Fig.5** was severely oxidized, although the higher carbon content on the nanofiber surface compared to the interior was curious, and the carbon content of just several % remained unchanged within the filament interior. The elemental composition in **Fig.5** suggested the existence of an amorphous compound with a composition relatively close to that of silicon dioxide. It is known that the oxygen in Nicalon fiber impairs mechanical properties at high temperature, because the oxygen is removed as CO gas, resulting in defects in the fiber¹⁴⁾.

In contrast to the above, the carbon content in the 1200 °C-monofilament increased gradually from the surface to the interior. The C : Si : O ratio was 1 : 1 : 1, corresponding to silicon oxycarbide. The composition was unchanged above etch times of ca. 800 sec (corresponding to 144 nm for SiO₂). The oxygen content in the 1200 °C-monofilament was far higher than the 13 atom % for Nicalon heated at 1200 °C¹⁵⁾. Thus, decreasing the oxygen content in these fibers is a major problem yet to be solved. Other open questions are why the elemental composition within each nanofiber is

constant and whether the carbon within the nanofibers can survive further oxidation. The results portrayed in **Figs.5** and **6** clearly indicated that the blend fiber had to be heated to the higher temperature to prepare nanofibers with high carbon content, by more complete transformation of PCS into oxidation-resistant inorganic material.

4. Conclusions

Phenolic resin containing fine polycarbosilane particles was spun, stabilized and heat-treated at 1000 °C or 1200 °C in an inert atmosphere, followed by oxidation using nitric acid to remove the matrix carbon. The nanofibers thus formed were recovered and their structures were examined, focusing in particular on the effects of temperature during the heat-treatment step. The 1200 °C-nanofibers with diameter less than 1 μm showed higher oxidation resistance, and had a smoother fiber surface than did the 1000 °C-nanofibers. The high oxidation resistance of the 1200 °C-nanofibers gave rise to a smaller specific surface area of 44 m²/g against 288 m²/g for the 1000 °C-nanofibers. Quantitative elemental analysis using XPS showed that the 1200 °C-filaments contained about 30 atom % carbon, whereas the carbon content of 1000 °C-filaments was just a few %. High-temperature heating was required to prepare highly oxidation resistant nanofibers with a large amount of carbon.

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