

Preparation of SiC/Ti(C,N) Ceramic Fibers by Sol-Gel Process and Carbothermal Reduction-Nitridation Reaction

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Using tetraethoxy silane, tetrabutyl titanate and sucrose as raw materials, TiO₂/SiO₂/sucrose hybrid fibers were prepared *via* sol-gel method associated with drawing process. The carbothermal reduction-nitridation reaction of the hybrid fibers was carried out under nitrogen atmosphere in the temperature range from 800-1500 °C. Fourier transfer infrared spectroscopy, thermalgravimetry, X-ray diffraction and scanning electron microscopy were employed to investigate the microstructure variation and reaction mechanism of the hybrid fiber in the carbothermal reduction-nitridation process. The results showed that Ti (C, N) formed at *ca.* 1200 °C and the formation temperature of SiC was about 1400 °C. SiC/Ti (C, N) composite ceramic fibers were finally produced at 1500 °C.

Key Words: Sol-gel process, Hybrid fibers, Carbothermal reduction-nitridation.

INTRODUCTION

Sol-gel process is well known as a chemical synthesis method for the preparation of inorganic-organic hybrid materials¹⁻³. By control of structure and interaction between the oligomeric or colloidal units, materials with different shapes of bulks, films and fibers can be prepared^{4,5}.

Recently, numerous efforts have been devoted to the preparation of inorganic-organic hybrid continuous fibers *via* sol-gel method⁶⁻⁹. Those novel fibers present excellent properties, such as superior heat-resistance and modified chemical-resistance. Moreover, those hybrid fibers have been carried out carbothermal reduction as precursors to prepare continuous SiC, Si₃N₄, ZrC and Si-Zr-C ceramic fibers¹⁰⁻¹³. In our previous work, precursors of SiC fiber that derived from SiO₂/sucrose hybrid sols had been obtained by sol-gel method¹⁴.

One of the advantages of the inorganic-organic hybrid route to fabricate ceramic fibers is that the ceramic fibers can be produced without cure of the precursors. Therefore, the fabrication of ceramic fibers can be simplified remarkably. As a typical carbide fiber, Si-Ti-C-O fiber has been commercially produced under the trade name of "Tyranno". Introduction of Ti into SiC fiber improves oxidation resistance and endows electrical performances that are different from those of SiC fiber^{15,16}.

In this study, a two-step method was employed to fabricate SiC/Ti(C,N) ceramic fibers. SiO₂/TiO₂/sucrose hybrid fibers were first prepared *via* sol-gel method and drawing process

using tetraethoxy silane (TEOS), tetrabutyl titanate (TBT) and sucrose as raw materials. Then, the hybrid fibers were heated at different temperatures (800-1500 °C). SiC/Ti(C,N) ceramic fibers were finally produced by carbothermal reduction-nitridation (CRN) at 1500 °C. The reaction mechanism and microstructure variation of the fibers in the carbothermal reduction-nitridation process were investigated.

EXPERIMENTAL

Preparation of SiO₂/TiO₂/sucrose hybrid fibers: The chemical reagents used in the experiments, tetraethoxy silane (TEOS), tetrabutyl titanate (TBT), sucrose, acetyl acetone (AcAc), ethanol (EtOH) and hydrochloric acid (HCl) were all analytical grade. The water was deionized.

Stoichiometric tetrabutyl titanate, acetyl acetone, EtOH, HCl (0.1M) and H₂O (TBT:AcAc:EtOH:HCl:H₂O = 1.0:0.5:4.0:0.01:2, mol ratio) were added successively into a 250 mL three-neck glass-flask with a condenser and a stirrer. The mixture was kept under stirring at ambient temperature for 1 h. Then a yellow transparent TiO₂ sol was obtained. TEOS, EtOH, HCl(0.1M) and H₂O (TEOS:EtOH:H₂O:HCl = 1.0:4.0:2.0:0.01, mol ratio) were added successively into another 250 mL three-neck glass-flask with constant stirring, the mixture was kept at ambient temperature for about 2 h. Then a transparent SiO₂ sol was prepared.

The SiO₂ sol was poured into TiO₂ sol slowly, with a mol ratio of SiO₂/TiO₂ at 1:1. The mixed sol was vigorously stirred at 60 °C for *ca.* 2 h. Thus a TiO₂/SiO₂ sol was made.

The sucrose solution (50 %, mass ratio) was finally added into the hybrid sol with a mol ratio of sucrose/Si/Ti at 1:2:2, so that the atomic ratio of carbon in sucrose to (Si + Ti) in hybrid sol at 3:1. The mixed solution was stirred for 1 h at 60 °C, finally, a SiO₂/TiO₂/sucrose hybrid sol was prepared. TiO₂/SiO₂/sucrose hybrid fibers were prepared by drawing process¹⁴.

Preparation of SiC/Ti(C,N) ceramic fibers: The hybrid fibers were placed in alumina boats. The boats were then placed into a tube furnace and heated at 800, 1000, 1200, 1400 and 1500 °C for 2 h under nitrogen atmosphere for carbothermal reduction-nitridation, respectively. The heating rate was 10 °C/min.

Characterizations: SEM images were observed by a SIRION 200 field emitted SEM equipment. FTIR spectra were recorded on a Nicolet-IR200 FTIR spectrometer with a resolution of 1 cm⁻¹. TG analysis were performed on a Shimadzu DTG-60H thermogravimetric analyzer under nitrogen atmosphere at a heating rate of 10 °C/min. XRD analysis were performed on a D/Max-rB XRD equipment using CuK_α radiation.

RESULTS AND DISCUSSION

Structure and performance of the hybrid fiber

FTIR spectra: The FTIR spectra of the SiO₂/TiO₂/sucrose hybrid fiber (Fig. 1a), SiO₂/TiO₂ gel fiber (Fig. 1b) and sucrose (Fig. 1c) are presented in Fig. 1. The band at 1135 cm⁻¹ is attributed to stretching vibration of C-O-C. The broad band around 3600-3200 cm⁻¹ arise from the stretching vibration of hydroxyl group. The absorption bands around 2940, 1430 and 1360 cm⁻¹ are assigned to the stretching and bending vibration of C-H groups. Two intense bands at 1580 and 1535 cm⁻¹ are ascribed to the stretching vibration of C=O and C=C due to acetyl acetone bound to titanium ions¹⁷.

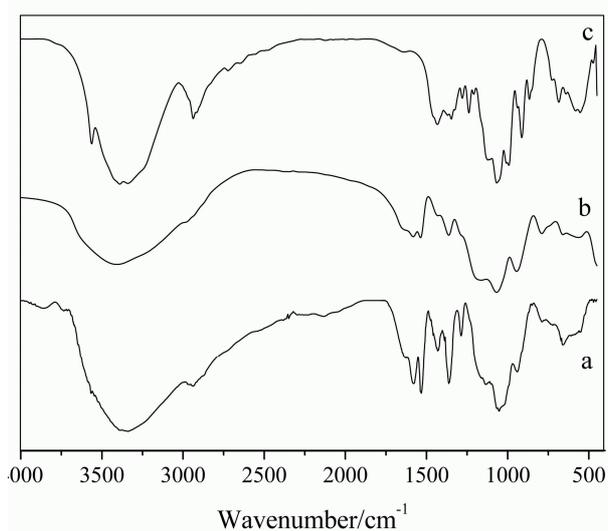


Fig. 1. FT-IR spectra of samples (a) SiO₂/TiO₂/sucrose hybrid fiber, (b) SiO₂/TiO₂ gel fiber, (c) sucrose

The bands around 1053 and 790 cm⁻¹ correspond to anti-symmetric and symmetric stretching vibration of Si-O-Si^{17,18}. The bands at 659 and 550 cm⁻¹ are assigned to stretching vibration of Ti-O-Ti¹⁸. These signals suggest the formation of

titanium oxide and silicon oxide gel networks which were caused by the hydrolysis and condensation of TEOS and TBT, respectively. The band at 941 cm⁻¹ is attributed to the antisymmetric stretching vibration of Si-O-Ti^{17,18}, which demonstrates the interaction between TiO₂ and SiO₂.

XRD pattern: XRD patterns of sucrose and SiO₂/TiO₂/sucrose hybrid fiber are shown in Fig. 2. Intense diffraction peaks can be observed in Fig. 2a, implying that pure sucrose is a well crystallized material. On the other hand, only two broad peaks centered around 25.5° and 45.0° (2θ) can be detected in Fig. 2b, which suggests that SiO₂/TiO₂/sucrose hybrid fiber is amorphous. It is deduced that the crystallization of sucrose was limited by the SiO₂/TiO₂ gel network.

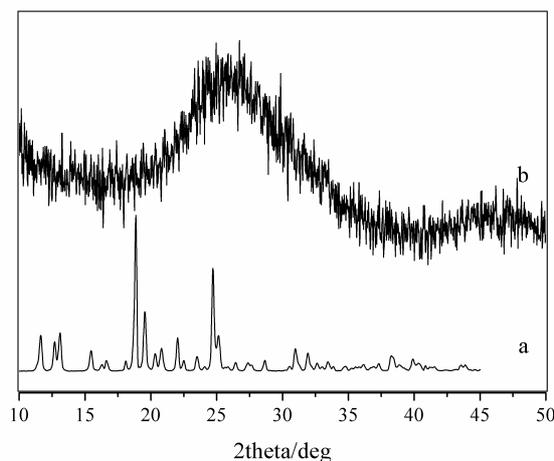


Fig. 2. XRD pattern of samples (a) sucrose, (b) SiO₂/TiO₂/sucrose hybrid fiber

TG curves: TG curves of sucrose and SiO₂/TiO₂/sucrose hybrid fiber are presented in Fig. 3. As shown in Fig. 3a, pure sucrose shows poor heat resistance with a residual rate of mass about 15.4 %. For SiO₂/TiO₂/sucrose hybrid fiber (Fig. 3b), three degradation steps are observed. The first step is from 40-232 °C with the mass loss about 16.2 %. That is mainly caused by the evaporation of residual small molecules (EtOH, BuOH, AcAc, H₂O and HCl) which derived from both raw materials and condensation products of hydroxyl and alkoxy group. The second step is between 231 and 424 °C, which is associated with the cleavage of C-O and C-H bonds of sucrose. Mass loss at this stage is about 17.8 %. The third step is from 424-800 °C, which arise from further decomposition of sucrose in the fiber, with the mass loss about 3.2 %. The final residue rate of mass is 62.8 %, which is much higher than the theoretical mass ratio of SiO₂/TiO₂.

The results of TG analysis suggest that the heat resistance of sucrose was modified by SiO₂/TiO₂ gel networks remarkably. The increased content of carbon residue in the hybrid fiber is important to the formation of SiC and Ti(C,N) during the carbothermal reduction-nitridation reaction.

Microstructure variation of the fiber in carbothermal reduction-nitridation reaction

FTIR spectra: The FTIR spectra of the hybrid fiber heated in the temperature range (800-1500 °C) are shown in Fig. 4. For the fiber heated at 800 °C (Fig. 4a), absorption bands

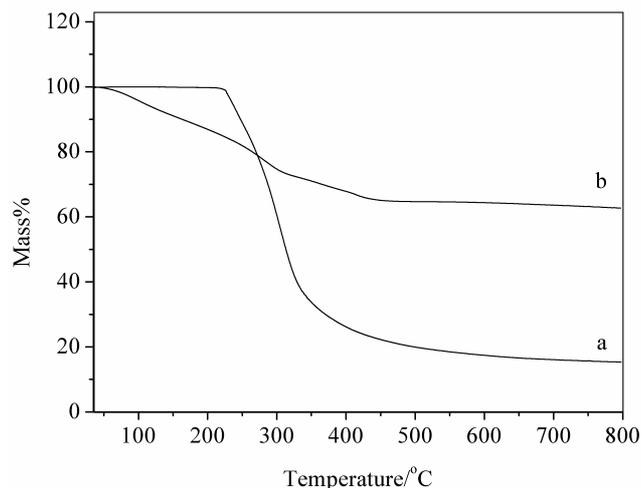


Fig. 3. TG curves of samples (a) sucrose, (b) SiO₂/TiO₂/sucrose hybrid fiber

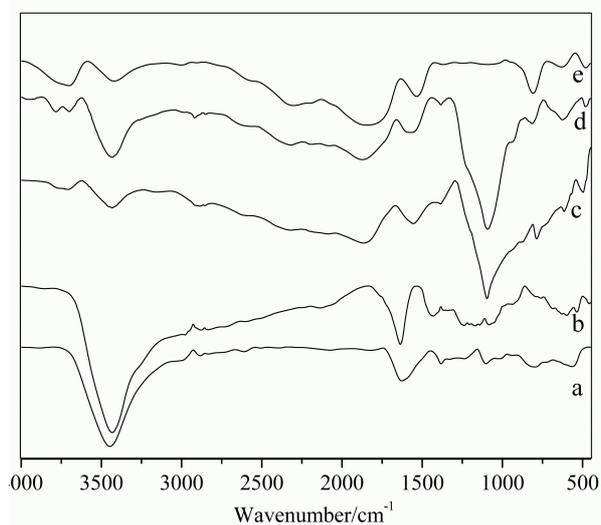


Fig. 4. FT-IR spectra of fiber heated at different temperatures (a) 800 °C, (b) 1000 °C, (c) 1200 °C, (d) 1400 °C, (e) 1500 °C

around 1100 and 795 cm⁻¹ arise from Si-O-Si. The broad band around 650-500 cm⁻¹ corresponds to Ti-O bond of anatase. When the heating temperature was kept at 1000 °C, as shown in Fig. 4b, two new bands appeared at 595 and 535 cm⁻¹, which are attributed to Ti-O bond of rutile¹⁹. For the fiber heated at 1200 °C (Fig. 4c), a relative intense band appeared around 1096 cm⁻¹, which suggests the existence of SiO₂. The bands of rutile phase TiO₂ at 595 and 535 cm⁻¹ disappeared, while new bands at 615 and 495 cm⁻¹ can be detected obviously, which correspond to Ti-N and Ti-C bond, respectively^{20,21}. For the fiber heated at 1400 and 1500 °C (Fig. 4d-e), new band around 815 cm⁻¹ is detected, which is ascribed to the stretching vibration of Si-C bond²². With the increase of the heat treatment temperature, the absorption bands of Si-O-Si disappeared while that of Si-C becomes intense gradually.

In general, according to the FTIR spectra, the reaction mechanism of the hybrid fiber in the carbothermal reduction-nitridation reaction can be deduced. Firstly, at 800 °C, TiO₂ gel network converted to anatase phase. When the heat

treatment temperature was kept at 1000 °C, anatase phase of TiO₂ began to transform to rutile phase. The carbothermal reduction-nitridation reaction of TiO₂ mainly occurred in the temperature range from 1000-1200 °C. Ti(C,N) could be detected at 1200 °C. When the temperature was kept above 1400 °C, the reduction reaction of SiO₂ occurred and SiC began to form gradually. The hybrid fiber finally converted to SiC/Ti(C,N) ceramic fiber when the heat treatment temperature was kept at 1500 °C.

XRD pattern: The crystalline phase transition of hybrid fiber in the carbothermal reduction-nitridation reaction is investigated by XRD analysis and the XRD patterns are shown in Fig. 5. Only anatase phase TiO₂ is observed in the XRD pattern of fibers heated at 800 °C (Fig. 5a). Rutile phase TiO₂ formed at 1000 °C (Fig. 5b). Well crystallized SiO₂ which correspond to α -cristobalite can be detected when the heat treatment temperature reached to 1200 °C. Peaks of both anatase and rutile phase TiO₂ disappeared at the same temperature while several new peaks are detected, which indicate the formation of Ti(C,N) crystalline (JCPDS No. 76-2484). After heated at 1400 °C for 2 h, weak peaks around 35.8°, 60.0° and 72.0° are observed, which are ascribed to β -SiC (JCPDS No. 73-1708). The intensity of peaks which correspond to α -cristobalite decreases while that of Ti(C,N) increases with the heating temperature elevated from 1200-1500 °C. Only Ti(C,N) and β -SiC can be detected in Fig. 5e as the temperature kept at 1500 °C.

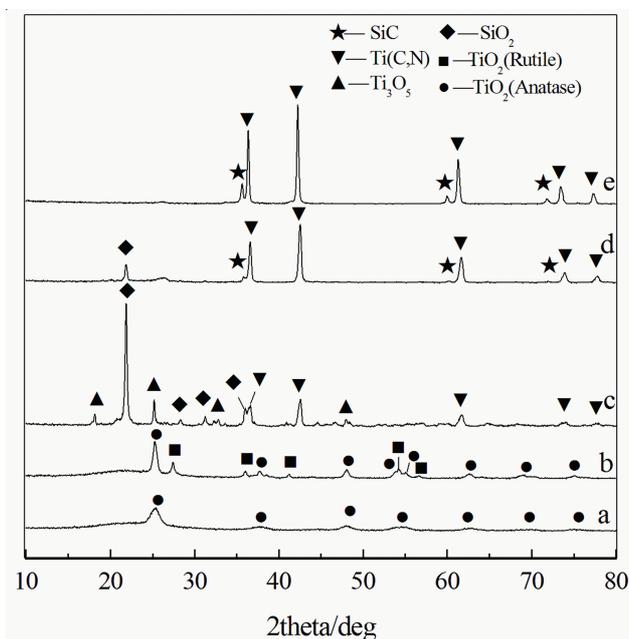


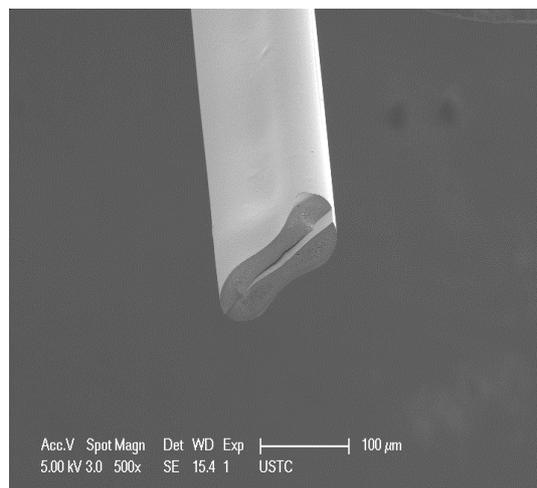
Fig. 5. XRD patterns of fiber heated at different temperatures (a) 800 °C, (b) 1000 °C, (c) 1200 °C, (d) 1400 °C, (e) 1500 °C

The results of XRD patterns and FTIR spectra were overall coincidental. They all confirmed the reaction mechanism and microstructure variation of the hybrid fiber in the carbothermal reduction-nitridation reaction.

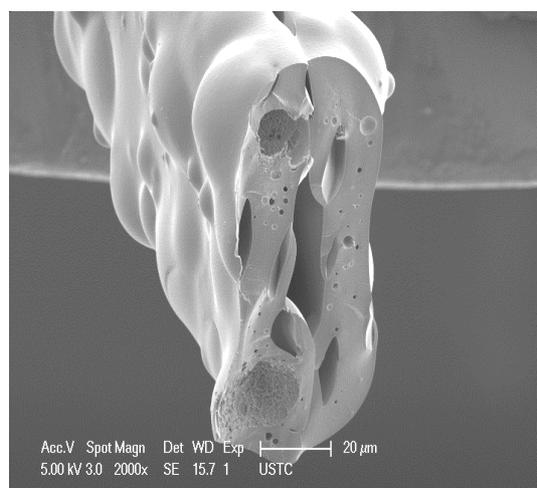
The phase transition temperature of TiO₂ from anatase to rutile has been reported, which is about 500-600 °C¹⁹. It should be noted that in the present work, the transition temperature is

much higher. The difference is resulted from the existence of silica and pyrolysis products of sucrose. The homogeneous $\text{SiO}_2/\text{TiO}_2$ gel network in the hybrid fiber influenced the crystallization and phase transition of TiO_2 significantly. With the increase of the heat treatment temperature from 1200-1500 °C, the diffraction peaks which correspond to $\text{Ti}(\text{C},\text{N})$ shift to low 2θ angle gradually. This minor variation is caused by the increase of TiC content in solid solution²³.

SEM images: The SEM micrographs of $\text{SiO}_2/\text{TiO}_2/\text{sucrose}$ hybrid fiber and the fiber heated at 1500 °C are presented in Fig. 6. As shown in Fig. 6a, the hybrid fiber has a smooth and uniform surface with a width about 120 μm , which indicates that the hybrid sol has excellent spinnability. After being heated at 1500 °C (Fig. 6b), the hybrid fiber converted to porous fiber with many pores in the internal and bubbles on the surface. That is resulted from the evaporation of trapped volatile compounds. During the carbothermal reduction reaction of SiO_2 ²², gaseous intermediate of SiO is also an important factor for the micromorphology variations of fiber. According to the SEM images, the fiber shape was kept well in the carbothermal reduction-nitridation process.



(a)



(b)

Fig. 6. SEM photographs of hybrid fiber (a) green hybrid fiber, (b) hybrid fiber heated at 1500 °C

Conclusion

$\text{SiO}_2/\text{TiO}_2/\text{sucrose}$ hybrid fibers were prepared by sol-gel process and drawing method. Novel $\text{SiC}/\text{Ti}(\text{C},\text{N})$ ceramic fibers were then prepared by carbothermal reduction-nitridation reaction using the hybrid fibers as precursors. $\text{Ti}(\text{C},\text{N})$ and SiC crystalline formed at about 1200 and 1400 °C, respectively. The hybrid fiber was converted into $\text{SiC}/\text{Ti}(\text{C},\text{N})$ ceramic fiber at 1500 °C and the morphology of the fiber was kept well.

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