



2012 International Conference on Solid State Devices and Materials Science

Large-scale Synthesis of SiBOC Fibers Produced by Electrospinning

Xia Li ^a*, G Wen ^{a,b}, Tao Zhang ^a, Long Xia ^b, Bo Zhong ^b, Shaoyu Fan ^c

^aSchool of Materials Science and Engineering, Harbin Institute of Technology, Harbin 150001, China

^bSchool of Materials Science and Engineering, Harbin Institute of Technology (Weihai), Weihai 264209, China

^cCollege of mechanical and electrical engineering, Weifang technical college, Weifang 262700, People's Republic of china

Abstract

Silicon oxy carbide (SiOC) glasses have received great attention due to its broad applications. But it didn't have perfect thermo stability. So this research tries to introduce element B to increase this stability. SiBOC gel fabricated from single-source polyborosiloxanes which are synthesized from polymethylethoxysiloxane (PMES) and B(OH)₃ by a sol-gel process, SiBOC fibers have been obtained by electrospinning. And SiBOC ceramic fibers gotten with perfect thermo stability.

© 2012 Published by Elsevier B.V. Selection and/or peer-review under responsibility of Garry Lee

Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

Keywords: SiBOC fibers, sol-gel method, Electrospinning, heart treatment.

1. Introduction

Silicon oxy carbide (SiOC) glasses have received great deal of attention due to their enhanced chemical, mechanical and thermal properties compared with pure silica. [1-3] It is believed that the enhancement is attributed to the incorporation of carbon into silicate glasses which strengthens the molecular structure. SiOC fibers have been fabricated by sol-gel method and polymer-derived ceramic route.[4,5] However, the high-temperature decomposition of SiOC glasses, which occurs at temperature above 1350°C due to carbon thermal reduction between silica and carbon,[6] results in significant weight loss and dramatic deterioration of mechanical properties. Thus, enhancing the thermal stability of SiOC glasses is still an ongoing task. Riedelet al.[7] and Kroke et al.[8] reported that boron doped silicon

* Corresponding author. Tel.: +086-0631-5687390; fax: +086-0631-5687393.

E-mail address: lxym_007@163.com.

carbon nitride (SiCNB) glasses got the improved thermal stability properties, which greatly inspired the SiOC glasses researchers. The incorporation of boron into silicon oxycarbide network was found to inhibit the formation of cristobalite [9,10] and lead to the growth of $[B(OSi)_3]$ units, reduction of $[SiO_4]$ units and enhancement of SiC crystallization. [11,12] The most important effect is that the decomposition temperature of boron addition silicon oxycarbide glasses increases at least up to $1400^\circ C$. [11,13] Therefore, the SiBOC ceramic products, including fibers, derived from boron addition silicon oxycarbide are promising candidates for high temperature applications. [14,15]

Ceramic fibers are a new lightweight refractory that widely used in demanding mechanical properties and good resistance to high components, including ablative materials (such as spacecraft re-entry heat shield, rocket nose cone, nozzle, vents and partitions, etc.). A large number of methods have already been demonstrated for generating ceramic fibers. Among these methods, e-spinning seems to provide the simplest approach. In comparison with other spinning techniques e-spinning utilizes an electric field for drawing the fibers. E-spinning produces non-woven fibers and has been shown to produce many “one-dimensional” shapes including fibers, ribbons, filled and hollow tubes, all having large specific surface areas. For the last 70 years, it was mainly used for making polymer fibers and has warranted several reviews for its broad applicability in producing polymer nanofibers.¹⁶⁻¹⁹ In this work, SiBOC gel fibers have been successfully obtained by e-spinning. SiBOC gel fabricated from single-source polyborosiloxanes which are synthesized from polymethylethoxysiloxane (PMES) and $B(OH)_3$ by a sol-gel process, and SiBOC ceramic fibers have been obtained by electrospinning. The morphological change, chemical mechanism and structural evolution of the fibers starting from gels to ceramics during heat treatment are investigated.

In addition, the oxidative stability behavior between $800^\circ C$ and $1300^\circ C$ is studied by X-ray diffraction and Raman spectroscopy to obtain the structural information on the various SiBOC ceramic fibers.

2. Experimental

The linear polymethylhydrogen siloxane (PMHS), $(CH_3)_3Si(CH_2(H)SiO)_m$, was purchased from Shinetsu Chemical Co., Ltd. Absolute ethyl alcohol, ethylenediamine and boric acid were supplied by Tianjin Kermael Chemical Reagents Development Centre, China. All the reagents were used as received without further purification. The synthesis of hybrid borosilicate precursors was performed in two steps: preparation of PMES and synthesis of polyborosiloxane gel by sol-gel method. 3ml of ethylenediamine was added into the mixture of 1000ml of PMHS and 1200ml of ethanol under magnetic stirring. The dehydrogenation reaction between PMHS and ethanol under catalysis of ethylenediamine was carried out at ambient temperature for 20 days, which was accompanied by the evolution of hydrogen. After elimination of residual ethanol under reduced pressure, 175ml of PMES was isolated as colorless liquid. The polyborosiloxane gels were synthesized according to the following procedure: PMES and $B(OH)_3$ were mixed and heated to $78^\circ C$. Then ethanol was gradually added into the mixture until the $B(OH)_3$ was completely dissolved under stirring. The transparent reaction mixture was kept under reflux at $78^\circ C$ until the precursor sol became viscous. Then, the sol was poured into plastic containers and was left open at ambient temperature for gelation. Five sets of sol solutions with B/Si molar ratio of 0.1, 0.2, 0.3, 0.4 and 0.6 were prepared. B/Si=0.2 was those as the e-spinning polymer for its perfect spinnability.¹⁵

A common hypodermic plastic syringe with a needle of 0.36mm inner diameter was used to contain the appropriate precursor solution. During e-spinning, a high voltage power supply (DW-N503-4ACCD, -50kV~0V) was used with its negative terminal connected with the syringe needle and a ground terminal connected with an aluminum foil. A graphite plate acting as the collector was placed on the aluminum foil. The distance between the syringe needle and the collecting graphite plate was set at 19cm.

3. Results and discussion

FT-IR spectra (Fig. 1) show that the PMES is characterized by different features with respect to PMHS. Most of the Si-H groups (2170 and 877cm^{-1}) are consumed in PMES, which is further confirmed by the evolution of hydrogen during the reaction process. A new band at 956cm^{-1} due to Si-OEt(Et=CH₃CH₂-) stretching vibration²¹ is observed in PMES. Three peaks are detected in the range of 2975 – 2890cm^{-1} : CH₃ asymmetric stretching at 2975cm^{-1} , the combination between the CH₃ symmetric and the CH₂ asymmetric stretching at 2923cm^{-1} , CH₂ symmetric stretching at 2890cm^{-1} , which confirm the presence of CH₃CH₂- groups in PMES. The strong Si-O absorption at 1080cm^{-1} with a shoulder at 1120cm^{-1} is characteristic of linear Si-O-Si chains. Molecular weights and molecular weight distributions of PMHS and PMES were examined by GPC. The molecular weights of PMES (M_w=3426, M_n=2815) are lower than that of PMHS (M_w=8361, M_n=5196). According to the number average molecular weight (M_n), the polymerization degrees of PMHS and PMES are about 80 and 30, respectively. Above results indicated that PMES was obtained based on dehydrogenation reaction.

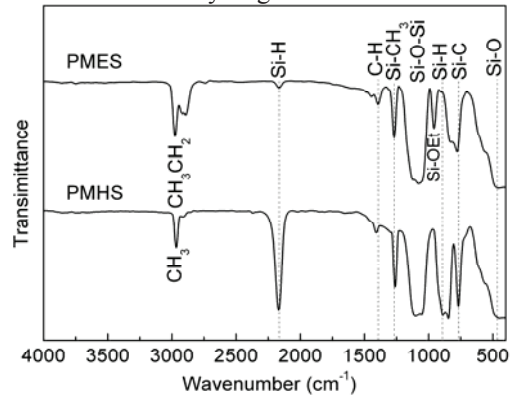


Fig.1 FT-IR spectra of PMES and PMHS

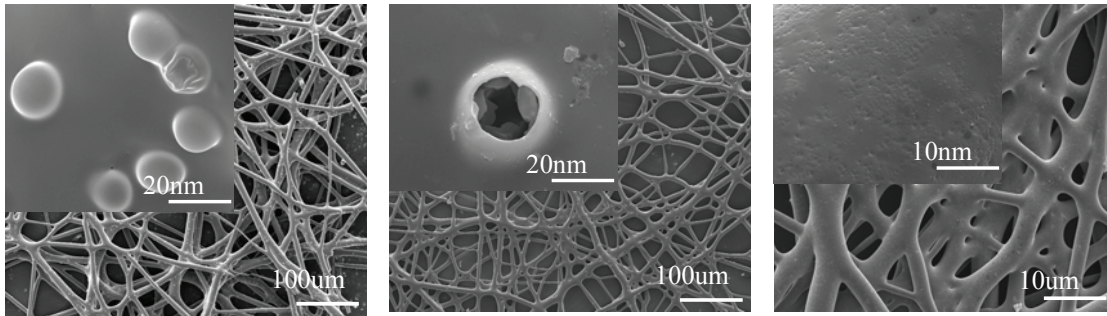


Fig.2 EDS of SiBOC ceramic fibers at different heat treatment temperature

(a)1300°C (b)1500°C (c)800°C

After spin by electrospinning equipments SiBOC fibers less than $5\mu\text{m}$ gotten. This fiber heated up from room temperature to 140°C for 1h is $2^\circ\text{C}\text{min}^{-1}$ in a high temperature tube furnace with the protecting of NH₃. Then form 140°C to 1700°C for 1h is 10°C^{-1} with the protecting of N₂. And then put the ceramic fibers into electric stove with out any protect gas. The temperature of stove is 1000°C , 1300°C and 800°C .

Fig.2(a) images at 1300°C B₂O₃ in the SiBOC fibers transgress and air bubble came into been, at 1500°C (Fig.2(b))the air bubble break down. At 800°C, SiBOC ceramic fibers has excellent performance and rigidity.

Acknowledgments

Supported by National Natural Science Foundation of China, under Grant No. 50672018, National High Technology Research and Development Program of China under Grant No. 2007AA03Z340, Program of Excellent Team in Harbin Institute of Technology.

References

- [1] Sorarù GD, Modena S. Chemical durability of silicon oxycarbide glasses. *J Am Ceram Soc.* 2002;**85**: 1529-36.
- [2] Moysan C, Riedel R, Harshe R, Rouxel T, Augereau F. Mechanical characterization of a polysiloxane-derived SiOC glass. *J Eur Ceram Soc.* 2007;**27**: 397-403.
- [3] Bréquel H, Parmentier J, Walter S, Badheka R, Trimmel G, Masse S, et al. Systematic Structural characterization of the high-temperature behavior of nearly stoichiometric silicon oxycarbide glasses. *Chem Mater.* 2004;**16**: 2585-98.
- [4] Kamiya K, Katayama A, Suzuki H, Nishida K, Hashimoto T, Matsuoka J, et al. Preparation of silicon oxycarbide glass fibers by sol-gel method—effect of starting sol composition on tensile strength of fibers. *JSol-Gel Sci Technol.* 1999;**14**:95-102.
- [5] Yajima S, Hayashi, Omori J, Okamura K. Development of a silicon carbide fibre with high tensile strength. *Nature* 1976;**261**: 683-5.
- [6] Saha A, Raj R. Crystallization maps for SiCO amorphous ceramics. *Jam Ceram Soc.* 2007;**90**: 578-83.
- [7] Riedel R, Kienzle A, Dressler W, Ruwisch L, Bill J, Aldinger F.A silicoboron carbonitride ceramic stable to 2,000 degrees C. *Nature.* 1996;**382**: 796-8.
- [8] Kroke E, Li YL, Konetschny C, Lecomte E, Fasel C. Silazane derived ceramics and related materials. *Mater Sci Eng R.* 2000;**26**: 97-199.
- [9] Klonczynski A, Schneider G, Riedel R, Theissmann R. Influence of boron on the microstructure of polymer derived SiCO ceramics. *Adv Eng Mater.* 2004;**6**: 64-8.
- [10] Liebau V, Hauser R, Riedel R. Amorphous SiBCO ceramics derived from novel polymeric. *C R Chim.* 2004;**7**: 463-9.
- [11] Schiavon MA, Gervais C, Babonneau F, Soraru GD. Crystallization behavior of novel silicon boron oxycarbide glasses. *J Am Ceram Soc.* 2004;**87**: 203-8.
- [12] Peñalón-Alonso R, Mariotto G, Gervais C, Babonneau F, Sorarù GD. New insights on the high-temperature nanostructure evolution of SiOC and B-doped SiBOC polymer-derived glasses. *Chem Mater.* 2007;**19**: 5694-702.
- [13] Ischenko V, Pippel E, Woltersdorf J, Yappi BRN, Hauser R, Fasel C, et al. Influence of the precursor cross-linking route on the thermal stability of Si-B-C-O ceramics. *Chem Mater.* 2008;**20**: 7148-56.
- [14] Ngoumeni-Yappi R, Fasel C, Riedel R, Ischenko V, Pippel E, Woltersdorf J, et al. Tuning of the rheological properties and thermal behavior of boron-containing polysiloxanes. *Chem Mater.* 2008;**20**: 3601-8.
- [15] H.W. Bai, G. wen, X.X. Huang, Z.X. Han, B. Zhong, Z.X. Hu X.D. Zhang Synthesis and structural characterization of SiBOC ceramic fibers derived from single-source polyborosiloxane. *J.Euro Ceram Soc.* 2011; **39**: 931-40.
- [16] T. Subbiah, G. S. Bhat, R. W. Tock, S. Pararneswaran, and S. S. Ramkumar. Electrospinning of Nanofibers. *J. Appl. Polym. Sci.* 2005; **96**: 557-69.
- [17] M. M. Hohman, M. Shin, G. Rutledge, and M. P. Brenner. Electrospinning and Electrically Forced Jets. I. Stability Theory. *Phys. Fluids.* 2001;**13**: 2201-20.
- [18] M. M. Hohman, M. Shin, G. Rutledge, and M. P. Brenner. Electrospinning and Electrically Forced Jets. II. Applications. *Phys. Fluids.* 2001;**13**: 2221-36.

- [19] D. Li and Y. N. Xia. Electrospinning of Nanofibers: Reinventing the Wheel?. *Adv. Mater.* 2004;**16**: 1151–70 .
- [20] D. Li, T. Herricks, and Y. N. Xia. Magnetic Nanofibers of Nickel Ferrite Prepared by Electrospinning. *Appl. Phys. Lett.* 2003; **83**: 4586–8.