J Mater Sci (2010) 45:2670–2674
DOI 10.1007/s10853-010-4247-4

SiO_2/TiO_2 fibers from titanium-modified polycarbosilane

Xueyuan Tang · Yuxi Yu · Daxiang Yang

Received: 16 September 2009 / Accepted: 18 January 2010 / Published online: 19 February 2010

Abstract We developed a process for preparing SiO_2/TiO_2 fibers by means of precursor transformation method. After mixing PCS and titanium alkoxide, continuous SiO_2/TiO_2 fibers were fabricated by the thermal decomposition of titanium-modified PCS (PTC) precursor. The tensile strength and diameter of SiO_2/TiO_2 fibers are 2.0 GPa, 13 μm, respectively. Based on X-ray diffraction (XRD), scanning electron microscopy (SEM), and high resolution transmission electron microscopy (HRTEM) measurements, the microstructure of the SiO_2/TiO_2 fibers is described as anatase–TiO_2 nanocrystallites with the mean size of ~ 10 nm embedded in an amorphous silica continuous phase.

Introduction

Ceramic fibers used reinforcements in ceramic matrix composites (CMCs) provide the skeletal structure of CMCs and are major contributors to the composite's mechanical and physical properties [1–6]. Ceramic fibers fall into two broad categories: (1) non-oxide fibers, such as SiC; and (2) oxide fibers, such as aluminum oxide, mullite ($3Al_2O_3$–$2SiO_2$), and silica [1–8]. The sol–gel method is the most common method of producing oxide fibers. First a fiber precursor solution is filtered and concentrated to remove excess solvent, forming a viscous spin dope. Then, continuous filaments are extruded by spinning. The filaments are pyrolyzed to remove volatile components and then heat treated above 800 °C to crystallize and sinter the fiber [1]. Non-oxide fibers are generally derived from polymeric precursors, which often require complicated intermediate processing before they can be pyrolyzed into ceramic fibers [6–12]. As a class, polymer-derived SiC-based fibers are the strongest ceramic fibers, which use polycarbosilane (PCS) as a precursor. PCS, which is obtained by thermal rearrangement reaction of PDMS, is silicon containing polymer known as a good precursor for SiC fibers [8–15]. The PCS can be easily modified by chemical reactions with a metallic alkoxide to obtain new systems [14–23]. For example, polytitanocarbosilane, which is produced by a condensation reaction of PCS with titanium (IV) tetraalkoxide, transforms into a SiC/TiC ceramic during thermal decomposition in nitrogen atmosphere [14, 15]. Polyzirconocarbosilane, which is synthesized by a condensation reaction of PCS with zirconium (IV) acetylacetonate, is a precursor of commercial Tyranno ZM SiC ceramic fiber [16]. Polyaluminocarbosilane as a precursor of Tyranno SA SiC ceramic fiber was prepared by thermolysis of a mixture of PCS and aluminum acetylacetonate [21].

Recently, some researchers have shown that oxide fibers could be obtained using PCS precursor [11, 13, 17]. A type of SiO_2/TiO_2 fibers has been prepared by Ishikawa [17] through polytitanocarbosilane precursor. The strength of SiO_2/TiO_2 fibers obtained from PCS was markedly higher (>2.5 GPa) than that of ordinary sol–gel SiO_2/TiO_2 fibers (<1 GPa). Up to now, there are few reports on the

---

X. Tang · Y. Yu (✉)
Department of Materials Science and Engineering, College of Materials, Fujian Key Laboratory of Advanced Materials, Xiamen University, 361005 Xiamen, Fujian, China
e-mail: yu_heart@xmu.edu.cn

X. Tang · Y. Yu
Key Laboratory of Fire Retardant Materials of Fujian Province, Xiamen University, 361005 Xiamen, Fujian, China

D. Yang (✉)
State Key Laboratory for Remanufacturing, The Academy of Armored Forces Engineering, 100072 Beijing, China
e-mail: yangdaxiang@hotmail.com

preparation of silica fibers made from PCS polymer precursor. The detailed study of SiO_2 fiber from PCS precursor has not been disclosed. So, the aim of this work is to produce and characterize a continuous SiO_2/TiO_2 fiber from a titanium-modified PCS precursor (PTC) using the following approaches:

(a) Synthesis of a polycarbosilane–titanium alkoxide hybrid precursor,
(b) Spinning of the precursor in molten state,
(c) Maturing and air curing of the green fiber,
(d) Sintering and physcio-chemical characterization of the fiber.

Experimental procedure

The PCS was prepared using a route that had been previously reported [9]. The process involves two steps: (i) the partial conversion of PDMS into polysilacarbosilane (PSCS) under atmospheric pressure and (ii) the thermolysis condensation at 420 °C under atmospheric pressure of PSCS into PCS. The PTC hybrid precursors were synthesized from PCS and $Ti(OC_4H_9)_4$. 20 g PCS and 20 g $Ti(OC_4H_9)_4$ were dissolved in 500 mL xylene in an 2 L, three-neck round-bottom flask under nitrogen gas with vigorous stirring at 100 °C. The mixture temperature was maintained at 100 °C for 1 h, a clear solution was obtained, and then increased to 150 °C to remove the xylene. The solution turned from orange to dark blue. Finally, the temperature was increased to 200 °C, and the reaction was carried out for 5 more hours. PTC hybrid precursors with dark blue color were obtained. PTC was melt-spun at 165 °C, and then the spun fiber was matured in air at 100 °C for 100 h. After maturation, the fiber materials were thermally cured under air atmosphere with a ramp rate of 20 °C h^{-1} to 200 °C and a dwell time of 5 h. Finally, the cured fibers were thermally decomposed at 1200 °C for 1 h in air to obtain the SiO_2/TiO_2 fibers.

Fourier transform-infrared (FT-IR) spectra were recorded between 4000 and 400 cm^{-1} on a Nicolet-360 spectrometer by the KBr pellet method. Gel permeation chromatography (GPC) measurements were taken with Waters-244 (eluent: THF 1 ml min^{-1}, calibration with polystyrene standards). Thermogravimetric (TG, Hi-Res TGA 2950) analyses were conducted to examine the ceramic yield of PTC. Elemental analyses of the TiO_2/SiO_2 fibers were performed on polished cross-section by electron probe microanalysis (EPMA) using a Camebax 75 (Cameca) in the wavelength dispersion mode (thallium acid phthalate (TAP) crystal for Si Kα, pentaerytritole (PET) for Ti Kα and a multilayer pseudo crystal multilayer (PCII) for C Kα and O Kα) with standard (SiC, Ti, and SiO_2) whose compositions were assumed to be stoichiometric. The surface and crystal structure of the fibers were analyzed by using a scanning electron microscopy (SEM: JEOL JSM-6300) equipped with a WinEDS detector, capable of detecting elements ≥B and X-ray diffractometer (XRD: model Siemens D-500, Cu Kα). Transmission electron microscopy (Tecnai F30, Philips-FEI, Eindhoven, the Netherlands) was also used for microstructure examination. Tensile strength of the fibers was measured by single-filament method (JIS R 7601) with gage length 25 mm (Model 2045, Corp. Shanghai).

Results and discussion

The precursor PTC was characterized by FT-IR, GPC, and TGA. The average molecular weight of PTC is $\overline{Mn} = 2200$, with a polydispersity index $I\text{p} = 2.5$. The ceramic yield at 1200 °C in air is about 87%. The softening temperature of PTC is about 110 °C. The FT-IR spectra of PCS and PTC have been collected over the wavenumber range of 4000–400 cm^{-1}, however, only the 2500–500 cm^{-1} wavenumber region is displayed in Fig. 1. The absorption peaks at 2950 and 2900 cm^{-1} (C–H stretching), 2100 cm^{-1} (Si–H stretching), 1400 cm^{-1} (C–H deformation in $Si\text{-}CH_3$), 1355 cm^{-1} (CH_2 deformation in $Si\text{–}CH_2\text{–}Si$), 1250 cm^{-1} ($Si\text{–}CH_3$ deformation), 1020 cm^{-1} (CH_2 deformation in $Si\text{–}CH_2\text{–}Si$), and in the vicinity of 800 cm^{-1} ($Si\text{–}CH_3$ deformation and Si–C stretching) were seen, and these suggest that the PTC was composed of nearly the same Si–C skeleton as PCS. In addition, the characteristic absorption band at 1090 cm^{-1} (Ti–O–C) attributed to $Ti(OC_4H_9)_4$ was observed in the FT-IR spectrum of the PTC. In order to estimate the reaction degree of Si–H

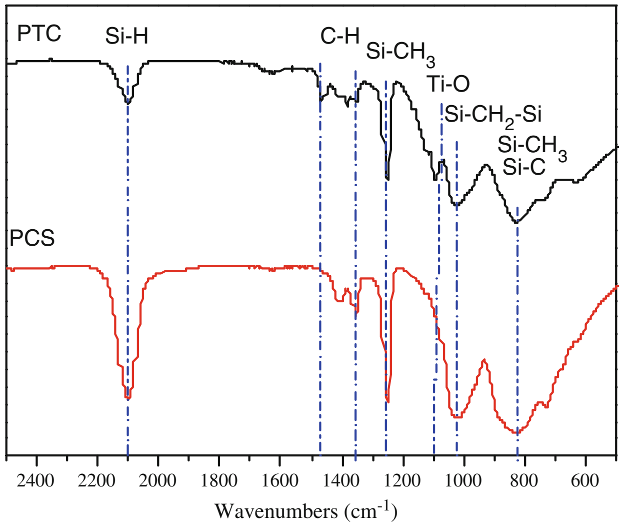
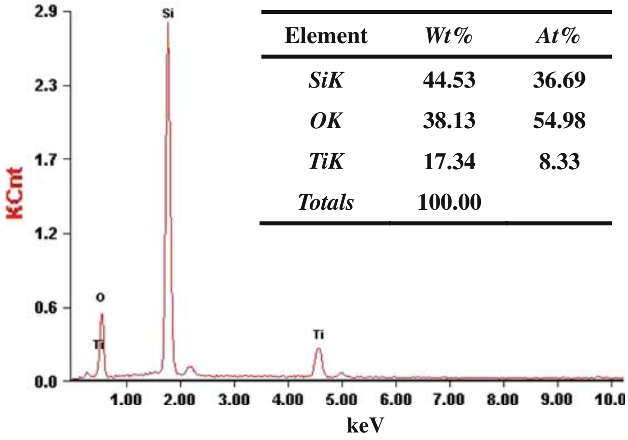


Fig. 1 FT-IR spectra of PCS and PTC

bonds, the Si–H bond content was calculated from the absorbency ratio of characteristic absorption peaks at 2100 and 1250 cm^{-1} (A_{Si-H}/A_{Si-CH_3}). The values of A_{Si-H}/A_{Si-CH_3} ratio were 0.696 for PCS and 0.297 for PTC. Decrease in the absorption peak at A_{Si-H}/A_{Si-CH_3} ratio and appearance of absorption peak at 1090 cm^{-1} in the spectrum of the PTC show the obvious difference in its structure from PCS. The above results imply that the PTC is not a simple mixture of PCS and $Ti(OC_4H_9)_4$, which is converted from the polymeric reaction of PCS with $Ti(OC_4H_9)_4$. These results about the reaction between PCS and $Ti(OC_4H_9)_4$ are consistent with the results reported from Okamura [19].

The chemical compositions of the SiO_2/TiO_2 fibers were analyzed by EDS. Their EDS spectrum and result of quantitative analysis by the Oxford Instruments INCA software package (INCA Energy 200) were shown in Fig. 2. As shown in Fig. 2, strong peaks for Si, Ti, and O could be found in the spectrum. The result of quantitative analysis (see the inset of Fig. 2) revealed that the Ti/Si atomic ratio was 0.23. The values are consistent with the theoretical Ti/Si atomic ratio (0.19). Figure 3 showed elemental dot-maps of O, Si, and Ti concentrations for a cross-section of SiO_2/TiO_2 fibers. All elements (O, Si, and Ti) were observed to homogeneously distribute in the fibers. And in the case of carbon element, it was not found. The skeleton of the precursor PTC was Si–C bonds, and consequently, carbon atoms existed in the main chain and the side chain. During the thermal decomposition of PTC green fiber in air, these carbon atoms were oxidized and are completely evolved from the fiber. The oxidation of PCS and $Ti(OC_4H_9)_4$ in PTC transformed into amorphous silica and TiO_2 with the generation of H_2O and CO_2, respectively [11–15, 19].

In Fig. 4, XRD patterns of SiO_2/TiO_2 fibers obtained from PTC were shown. The PTC green fibers pyrolyzed below 1200 °C give a broad diffuse hump at around $2\theta = 22.5°$, confirming an amorphous structure. The diffraction lines assigned to anatase become distinct with increasing heat treatment temperature. In 1200 °C XRD patterns, the broad diffraction peak at $2\theta = 22.5°$ is assigned to amorphous silica. The XRD pattern also exhibits one sharp peak and four small peaks corresponding to those of anatase–TiO_2 crystal, which are attributed to the (101), (111), (200), (211), and (204) plane of anatase–TiO_2 crystal [10]. These results show the microstructure of the PTC green fibers pyrolyzed at 1200 °C is mainly composed of anatase–TiO_2 along with amorphous silica. In TiO_2 fiber obtained by sol–gel method, anatase appeared on heat treatment at 150 °C and was converted into rutile above 700 °C. In particular, pure nanocrystalline anatase more



Element	Wt%	At%
SiK	44.53	36.69
OK	38.13	54.98
TiK	17.34	8.33
Totals	100.00	

Fig. 2 EDS spectrum and quantitative analysis result of the SiO_2/TiO_2 fibers

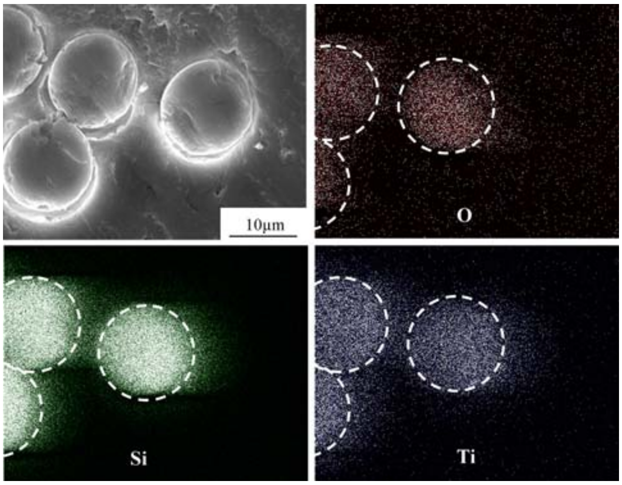


Fig. 3 Cross-section elemental dot-maps of the SiO_2/TiO_2 fibers. Shown are concentrations of O, Si, and Ti

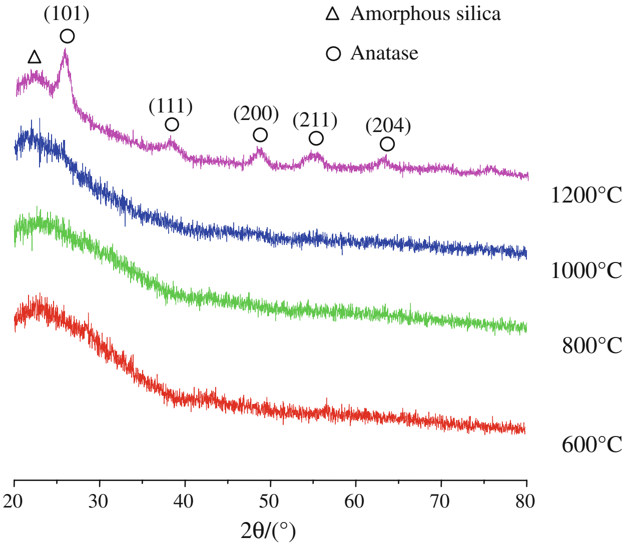


Fig. 4 Change in XRD patterns with heat treatment temperature in the fibers obtained from PTC in air

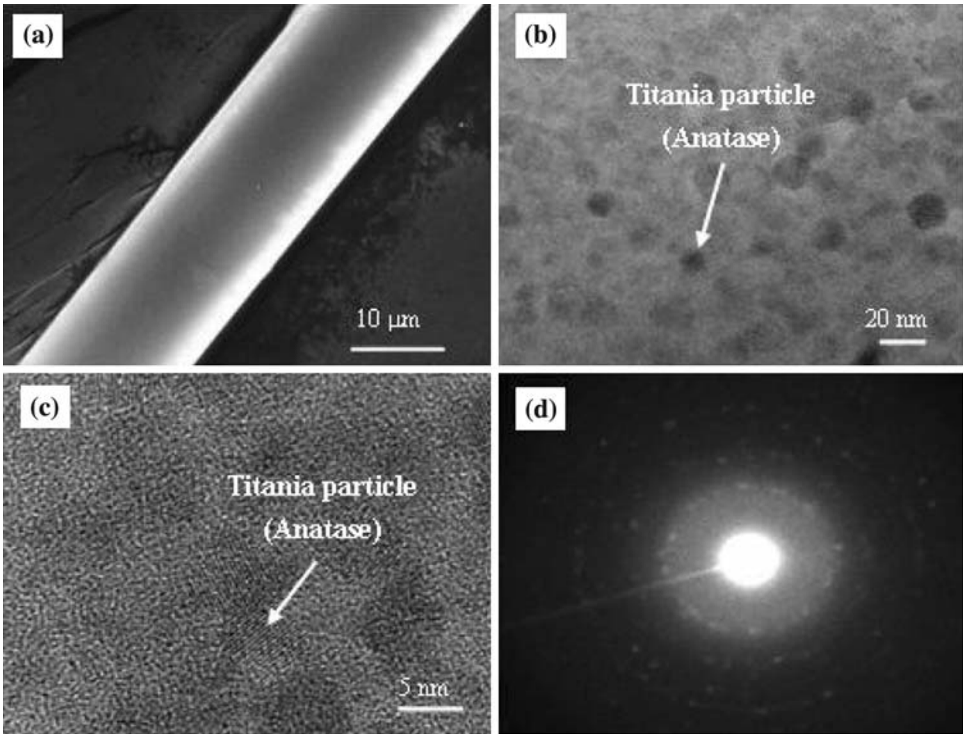


Fig. 5 SEM micrograph and TEM image of the SiO_2/TiO_2 fibers. **a** SEM micrograph of the surface. **b**, **c** TEM image of the SiO_2/TiO_2 fibers (**c** is enlargement of one part of **b**). **d** SAD pattern

easily converts to rutile at lower temperature (~500 °C) [12–14]. In our case, although this fiber was pyrolyzed at very high temperature (1200 °C), no obvious rutile phase could be observed. It is thought that the surrounding SiO_2 phase caused the stabilization of the anatase phase.

Figure 5 shows SEM micrograph and TEM image of SiO_2/TiO_2 fibers. The fibers have a very smooth surface without any observable flaws. The TEM images and corresponding SAD pattern show the SiO_2/TiO_2 fiber consists of titania crystal and amorphous continuous phase. It indicates titania nanoparticles embedded in an amorphous matrix and reveals that the mean size of nanoparticles is ~ 10 nm. This amorphous phase is concluded to be silica from the thermal decomposition of PTC in air. It is well known that, when pure PCS fibers are pyrolyzed in air, the fibers are oxidized first to amorphous silica and then the silica crystallizes to, probably α-quartz, eventually can not retain fiber shape [18–20]. However, the PTC green fibers were pyrolyzed at 1200 °C in air, the fiber shape could be kept. Therefore, the greater stability of the PTC precursors is due to the inhibition of the silica to crystallise due to the presence of the titanium. At the same time, the presence of TiO_2 nanoclusters in fibers also increases the viscosity preventing the collapse and the crystallization of the fibers. There are analogues to be found in the manufacture of other oxide systems used in fiber production [1].

The PTC can be continuously melt-spun and then matured and cured in air. By pyrolysis of the cured PTC fibers at temperatures above 400 °C in air, SiO_2/TiO_2 fibers can be obtained. The fibers obtained are colorless and transparent, and contain no carbon. Figure 6 shows the tensile strength of the SiO_2/TiO_2 fibers prepared by pyrolyzing at various temperatures. The tensile strength of the SiO_2/TiO_2 fibers increases as the pyrolysis temperature increases. The increase of tensile strength of the SiO_2/TiO_2 fibers with pyrolysis temperature is typical for polymer-derived ceramic fibers and is usually ascribed to the organic–inorganic transformation [17–20]. The SiO_2/TiO_2 fibers have the maximum values at 1200 °C. After the pyrolysis in air at 1200 °C, the PTC fibers shrank by a

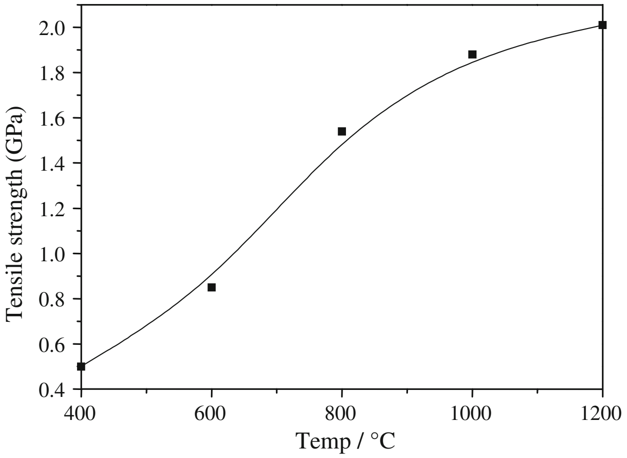


Fig. 6 The tensile strength of the SiO_2/TiO_2 fibers prepared by the pyrolyzing at various temperatures in air

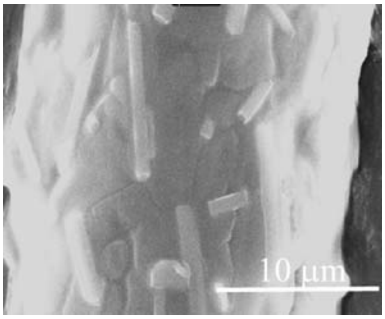


Fig. 7 SEM micrograph of the SiO_2/TiO_2 fibers prepared by the pyrolyzing at 1300 °C in air

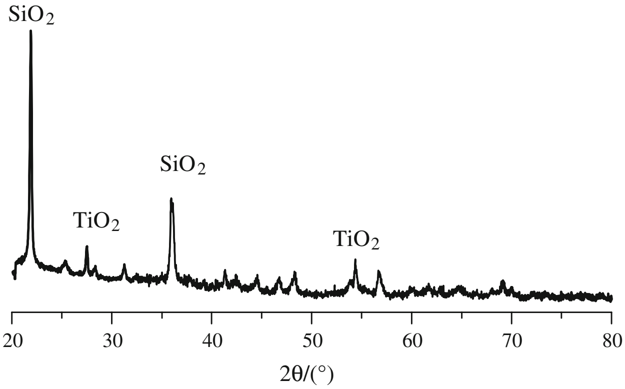


Fig. 8 XRD pattern of the SiO_2/TiO_2 fibers prepared by the pyrolyzing at 1300 °C in air

remarkable 35% from 20 to 13 μm in an average diameter. The high shrinkage of fibers indicates a high level of densification, which is also typical for polymer-derived ceramic fibers [9, 17–20]. Above 1300 °C heat treatment temperature, the SiO_2/TiO_2 fibers obtained were stuck to each other, so that measuring the mechanical properties of the fiber was difficult. Figure 7 shows the SEM micrograph of the SiO_2/TiO_2 fibers prepared by pyrolyzing at 1300 °C. It could be observed that the surface of the SiO_2/TiO_2 fibers from pyrolyzing at 1300 °C had an extremely rough surface on which many particles of 5–10 μm in size, presumably TiO_2 grain, had grown excessively during treatment. Figure 8 shows XRD pattern of the SiO_2/TiO_2 fibers prepared by the pyrolyzing at 1300 °C in air. The XRD pattern proved the nature of the crystalline phases in the SEM picture. Therefore, the decrease of the tensile strength above 1200 °C heat treatment temperature is considered to be related to grain coarsening.

Conclusions

On the basis of a precursor method using PCS, we developed a process for preparing SiO_2/TiO_2 fibers. This process treated the PTC precursor which was mixture of PCS and $Ti(OC_4H_9)_4$. The SiO_2/TiO_2 fibers were manufactured by melt-spinning PTC, maturing and curing in air the resulting fibers, followed by a final pyrolysis at 1200 °C in air. The tensile strength and diameter of the SiO_2/TiO_2 fibers were 2.0 GPa, 13 μm, respectively. The microstructure of the SiO_2/TiO_2 fibers can be described as anatase–TiO_2 nanocrystallites with the mean size of ~10 nm embedded in an amorphous silica continuous phase.

Acknowledgements This work was supported by the Natural Science Foundation for Young Scientists of Fujian Province, China (Grant No. 2009J05133) and Key Laboratory of Fire Retardant Materials of Fujian Province (Xiamen University), China (Grant No. 2009J1009).

References

1. DiCarlo JA, Yun HM (2005) In: Bansal NP (ed) Handbook of ceramic composites. Kluwer Academic Publishers, New York, p 33
2. Bunsell AR, Piant A (2006) J Mater Sci 41:823. doi:10.1007/s10853-006-6566-z
3. Laine RM, Babonneau F (1993) Chem Mater 5:260
4. Lipowitz J, Barnard T, Bujalski D, Rabe JA (1994) Comp Sci Technol 51:167
5. Chollon G, Aldacourrou B, Capes L, Pailler R, Naslain R (1998) J Mater Sci 33:901. doi:10.1023/A:1004395308173
6. Babonneau F, Sorarú GD, Thorne KJ, Mackenzie JD (1991) J Am Ceram Soc 74:1725
7. Sugimoto M, Shimoo T, Okamura K, Seguchi T (1995) J Am Ceram Soc 78:1013
8. Birot M, Pillot JP, Dunogues J (1995) Chem Rev 95:1443
9. Yajima S, Hayashi J, Omori M, Okamura K (1976) Nature 261:683
10. Yu YX, Tai JH, Tang XY, Guo YD, Tang M, Li XD (2008) Composites: Part A 39:1101
11. Ishikawa T (2004) Int J Appl Ceram Technol 1:49
12. Yu YX, Guo YD, Cheng X, Zhang Y (2009) J Mater Chem 19:5637
13. Ishikawa T (2005) Adv Polym Sci 178:109
14. Song YC, Feng CX, Tan ZL, Lu Y (1990) J Mater Sci Lett 9:1310
15. Song YC, Hasegawa Y, Yang SJ, Sato M (1988) J Mater Sci 23:1911. doi:10.1007/BF01115750
16. Hasegawa Y, Feng CX, Song YC, Tan ZL (1991) J Mater Sci 26:3657. doi:10.1007/BF00557131
17. Ishikawa T, Yamaoka H, Harada Y, Fujii T, Nagasawa T (2002) Nature 416:64
18. Ishikawa T, Yamamura T, Okamura K (1992) J Mater Sci 27:6627. doi:10.1007/BF01165946
19. Yamamura T, Ishikawa T, Shibuya M, Okamura K (1988) J Mater Sci 23:2589. doi:10.1007/BF01111919
20. Yamaoka H, Ishikawa T, Kumagawa K (1999) J Mater Sci 34:1333. doi:10.1023/A:1004506300754
21. Ishikawa T, Kohtoku Y, Kumagawa K (1998) Nature 391:773
22. Yu YX, Tang XY, Li XD (2008) Compos Sci Technol 68:1697
23. Bouillon E, Langlais F, Pailler R, Naslain R, Cruege F, Huong PV (1991) J Mater Sci 26:1333. doi:10.1007/BF00544474