Hierarchical structural silica-fiber-woven/mullite-whiskers material prepared by surface etching and gas-phase reaction

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Abstract

Hierarchical structural silica-fiber-woven/mullite-whiskers material was prepared through surface etching and gas phase reaction. In the material, the silica-fiber-woven served as the substrate, and a mass of mullite whiskers grew on the silica fibers through fluorine-catalyzed gas phase reaction (mixed AlF_3-SiO_2 powders were used as raw material). The silica-fiber-woven was first etched by fluorine-rich gas which was produced in the gas phase reaction, and the etching pits on the silica fibers offered nucleate sites for the mullite whiskers' growth. The volume density, tensile strength and thermal conductivity of the hierarchical structural silica-fiber-woven/mullite-whiskers material were 0.572g/cm^3, 0.441MPa and 0.1233W/m·k, respectively, indicating the suitability of the material for being used as heat-sealing/insulation gasket at high temperature.

Keywords: silica-fiber-woven; mullite whisker; hierarchical; heat-insulation

Heat-sealing/insulation materials had been extensively concerned in the fields of

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aerospace engineering, industry production and civil use [1]. They could be used between the components in the machines which were applied at high temperature. In order to satisfy the uses requirements, the heat-sealing/insulation materials should have low volume density, high thermal resistance, low thermal expansion coefficient, low thermal conductivity and proper mechanical strength [2-4]. Fibers which had excellent high-temperature properties were always used for preparing the heat-sealing/insulation materials. For example, Z.G. Hou et al [2] had prepared mullite-fibers/silica composite fibrous frameworks through TBA (tert butyl alcohol) -based gel-casting method. X. Dong et al [3] also reported mullite-fibers/silica-boron-glass composite frameworks which were prepared by infiltration method. Besides, the fibers could also be added in the aerogel to enhance the mechanical performance of the material, and some related work had been reported by J.J. Zhao et al [4] and J.J. Shi et al [5]. In addition, for filling some narrow gaps between the high-temperature components, the preparation of thin heat-sealing/insulation gaskets became much more significant. However, the methods used for preparing the bulk heat-sealing/insulation material that were reported in the mentioned references [2-5] were deemed to be unaccommodated for preparing thin heat-sealing/insulation gaskets.

It was known that the silica fibers were usually applied in high temperature circumstance, by possessing high thermal melting point, low thermal conductivity, low thermal expansion coefficient, high thermal shock resistance and good mechanical properties, etc [6, 7]. Silica-fiber-woven, which was prepared by continuous silica fibers through different knitting ways, could be applied as high temperature structural materials or as reinforcement in ceramic matrix composite materials (CMCs) [8-10]. Thus, in our present work, the silica-fiber-woven with thickness of ~1mm was used as matrix for preparing thin heat-sealing/insulation gasket. However, the very thin silica-fiber-woven was too soft/flexible which made it difficult to be handled with when using. For making the material more applicable, it was necessary to introduce some suitable rigid material into the silica-fiber-woven to balance the flexibility and rigidity. Besides, it would be desirable if the introduced rigid material could modify the properties of the silica-fiber-woven. It was known that, mullite whiskers as a kind of rigid material had excellent high-temperature properties, such as high temperature-resistance and low thermal conductivity, etc [11-13]. Therefore, we introduced the mullite whiskers into the silica-fiber-woven in our work for modifying the applicability and properties of the silica-fiber-woven.

In this work, hierarchical structural silica-fiber-woven/mullite-whiskers material was prepared through surface etching and gas phase reaction. In the preparation procedure, the silica-fiber-woven was placed in an airtight alumina crucible, and the mixed AlF_3-SiO_2 powders {[(mixed AlF_3-SiO_2 powders)/silica-fiber-woven]$_{mass}$=1/1, $(AlF_3/SiO_2)_{mole}$=3/1} were placed surround the silica-fiber-woven in the crucible. After being heat-treated at 1000°C for 2h, the hierarchical structural silica-fiber-woven/mullite-whiskers material was formed. (The detailed information of the preparation process and the test methods of the hierarchical structural silica-fiber-woven/mullite-whiskers material were depicted in Part 1 of the electronic supplementary information.)

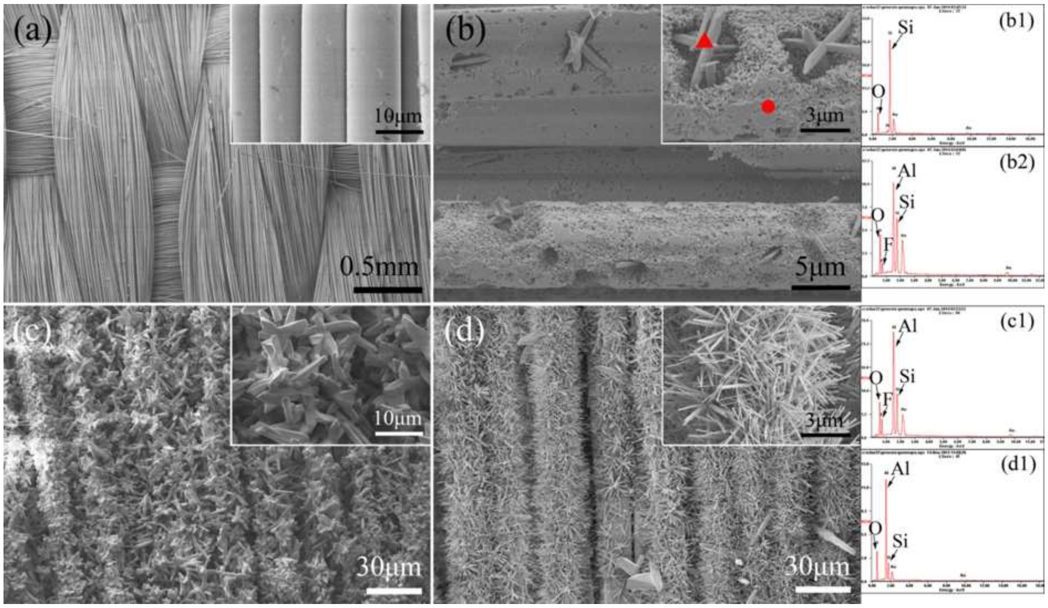

Fig.1 SEM images and EDS results, (a) silica-fiber-woven as substrate, (b) the sample that formed at 800°C, (c) the sample that formed at 900°C, (d) the hierarchical structural silica-fiber-woven/mullite-whiskers material that formed at 1000°C, (b1) EDS result of the point that was marked with "●" in Fig.1b, (b2) EDS result of the point that was marked with "▲" in Fig.1b, (c1) EDS result of the rod-like grains in Fig.1c, and (d1) EDS result of the whiskers in Fig.1d.

Fig.1 showed the microstructure of the silica-fiber-woven and the samples that formed at 800-1000°C. From Fig.1a, the silica-fiber-woven was uniformly knitted, and the surface of the silica fibers was smooth. From Fig.1b, a mass of etching pits formed on the silica fibers, besides, some rod-like grains grew from the etching pits. It was showed in Fig.1b1 that the etching pits were silica phase (SiO_2), and according to Fig.1b2, the rod-like grains were detected to be topaz ($Al_2SiO_4F_2$). When the heating temperature was raised to 900°C, the rod-like topaz grains grew densely on the silica fibers (Fig.1c and c1). From Fig.1d and d1, the topaz grains on the silica fibers all transformed into mullite whiskers. This microstructure changing process could also be clearly observed in the SEM images of the cross-section of the silica fibers in the samples which were heat-treated at 800-1000°C (Fig. S1).

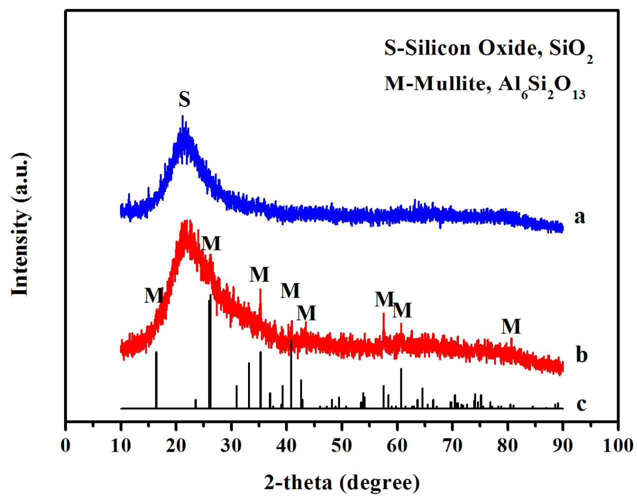

Fig.2 XRD patterns of the silica-fiber-woven (a) and the hierarchical structural silica-fiber-woven/mullite-whiskers material (b), and the standard pattern of mullite phase (PDF#15-0776) (c).

Fig.2 showed the XRD patterns of the silica-fiber-woven and the hierarchical structural silica-fiber-woven/mullite-whiskers material that formed at 1000°C. A large diffraction peak of silicon oxide (SiO_2, PDF#29-0085) existed in the XRD pattern of the silica-fiber-woven (Fig.2a). From Fig.2b, Mullite ($Al_6Si_2O_{13}$, PDF#15-0776) was detected in the hierarchical structural silica-fiber-woven/mullite-whiskers material. This was in accordance with the result that were showed in Fig.1d1. Besides, even if the hierarchical structural material was prepared at 1000°C, the crystallinity of silicon oxide in the silica-fiber-woven was still not changed obviously.

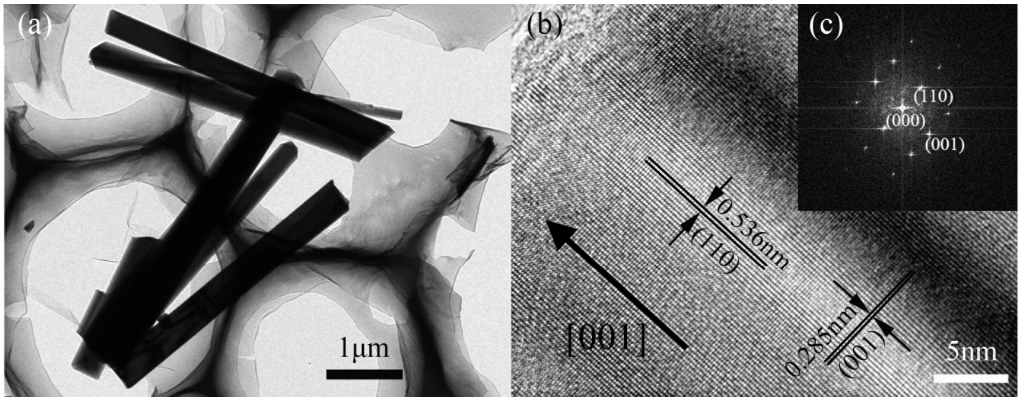

Fig.3 TEM images (a, b) of the mullite whiskers which were peeled off from the hierarchical structural silica-fiber-woven/mullite-whiskers material, and (c) was the mullite lattice's reciprocal lattice pattern by fast Fourier transform (FFT).

Fig.3 showed the TEM images and reciprocal lattice pattern (by fast Fourier transform) of the mullite whiskers that were peeled off from the hierarchical structural material. The mullite whiskers had diameter of 0.1-0.8μm (Fig.3a). Fig.3b showed the good crystallinity of the mullite whiskers, and the interplanar spacing that was measured in the TEM image was in accordance with the standard value in the PDF card (PDF#15-0776). In addition, it was detected from the reciprocal lattice pattern (Fig.3c) that the mullite whiskers elongated along the [001] direction. This was due to the crystal growth's intrinsic character of the mullite. It had been reported that, the stable mullite's orthorhombic structure consisted edge-shared AlO_6 octahedral chains, which aligned in the c-direction and was cross-linked by corner-shared $(Si,Al)O_4$ tetrahedral. Therefore, the mullite grains might grow faster in the direction that was parallel to the c-axis [14].

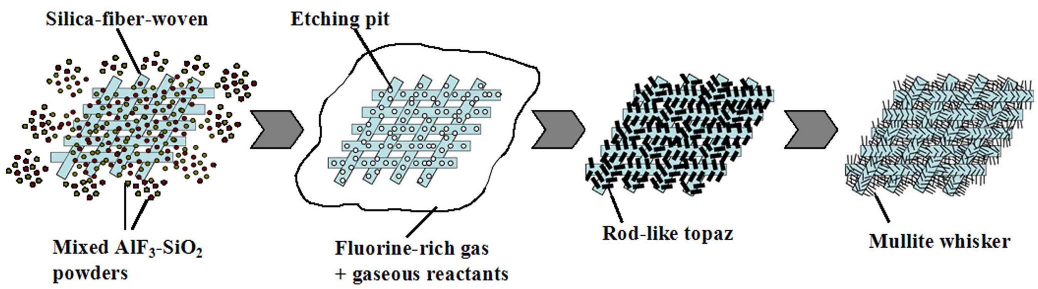

Fig.4 Schematic diagram, structure forming process of the hierarchical structural silica-fiber-woven/mullite-whiskers material.

The structure formation's schematic diagram of the hierarchical structural silica-fiber-woven/mullite-whiskers material was showed in Fig.4. At lower temperature, AlF_3 as raw material powders reacted with O_2 to form gaseous AlOF and fluorine-rich gas [15, 16]. The fluorine-rich gas diffused in the silica-fiber-woven and etched the silica fibers' surface (Fig.1b) (the completely etched sample which was composed of mullite whiskers was showed in Part 2 of the electronic supplementary information, and it could prove the etching process of the silica-fiber-woven in the heating procedure). The etching pits could offer nucleates sites for the secondary structures' growth [17]. Meanwhile, the SiO_2 powders transformed into gaseous SiF_4 under the catalysis of fluorine-rich gas [15]. Then, at higher temperature (800-900°C), gaseous reactants (AlOF and SiF_4) which diffused among the silica fibers deposited at the etching pits and reacted to form rod-like topaz grains. As the heating temperature rising to 1000°C, the topaz grains all transformed into mullite whiskers, thus, hierarchical structural silica-fiber-woven/mullite-whiskers material was formed.

Table 1 Volume density, tensile strength and thermal conductivity of the silica-fiber-woven and the hierarchical structural silica-fiber-woven/mullite-whiskers material.

Sample	Volume density (g/cm^3)	Tensile strength (MPa)	Thermal conductivity (W/m·k)
Silica-fiber-woven	0.774	9.399	0.1475
Hierarchical structural silica-fiber-woven/mullite-whiskers material	0.572	0.441	0.1233

The volume density, tensile strength and thermal conductivity of the silica-fiber-woven and the hierarchical structural silica-fiber-woven/mullite-whiskers material were listed in Table 1. The volume density of the hierarchical structural material was 0.572g/cm^3 which was obviously decreased compared with that of the silica-fiber-woven (0.774g/cm^3). This result had much intimate relationship with the surface etching of the silica fibers. However, the etching process also resulted in lower tensile strength (0.441MPa) compared with that of the silica-fiber-woven (9.399MPa). Besides, the growth of the rigid mullite whiskers increased the brittle character of the fibrous woven in some extent, and this also led to relatively lower tensile strength. Even so, the tensile strength of the hierarchical structural material was still desirable for meeting the uses requirements. Moreover, the thermal conductivity of the hierarchical structural material was 0.1233W/m·k at room temperature, which was obviously lower compared with that of the silica-fiber-woven (0.1475W/m·k). This was due to the mullite whiskers which were introduced into the silica-fiber-woven and helped to decrease the thermal conductivity of the material by lengthening the heat transfer route in the material [18]. It had been reported that, the increased heat transfer route could reduce the heat transfer rate in the material, and then decrease the thermal conductivity of the material [4, 5]. Besides, as the raw material powders (AlF_3+SiO_2) mass ratio increased in some extent, the mullite whiskers that grew on the silica fibers became larger, and the volume density/thermal conductivity/tensile strength were tested to be decreased (the detailed information was written in Part 3 of the electronic supplementary information).

In summary, hierarchical structural silica-fiber-woven/mullite-whiskers material was prepared by surface etching and gas phase reaction in this paper. Mixed AlF_3-SiO_2 powders were used as raw material powders. The silica fibers were first etched by the fluorine-rich gas which was produced in the gas phase reaction, and a mass of etching pits formed on the silica fibers. The etching pits offered nucleates sites for the secondary structures' growth in the gas phase reaction. Topaz rod-like grains grew at the etching pits at 800-900°C, and then they transformed into mullite whiskers at 1000°C. The mullite whiskers that were introduced into the silica-fiber-woven decreased the volume density and the thermal conductivity of the material. Moreover, the tensile strength of the hierarchical structural material was tested to be 0.441MPa which could satisfy the uses requirements. Therefore, the hierarchical structural silica-fiber-woven/mullite-whiskers material that possessed high heat-resistance, low volume density, low thermal conductivity and proper tensile strength was deemed to be suitable for being used as heat-sealing/insulation gasket at high temperature.

Acknowledgment:

The authors would like to acknowledge the National Natural Science Foundation of China (Project No. 51172156 and Project No.51272171) for financial support.

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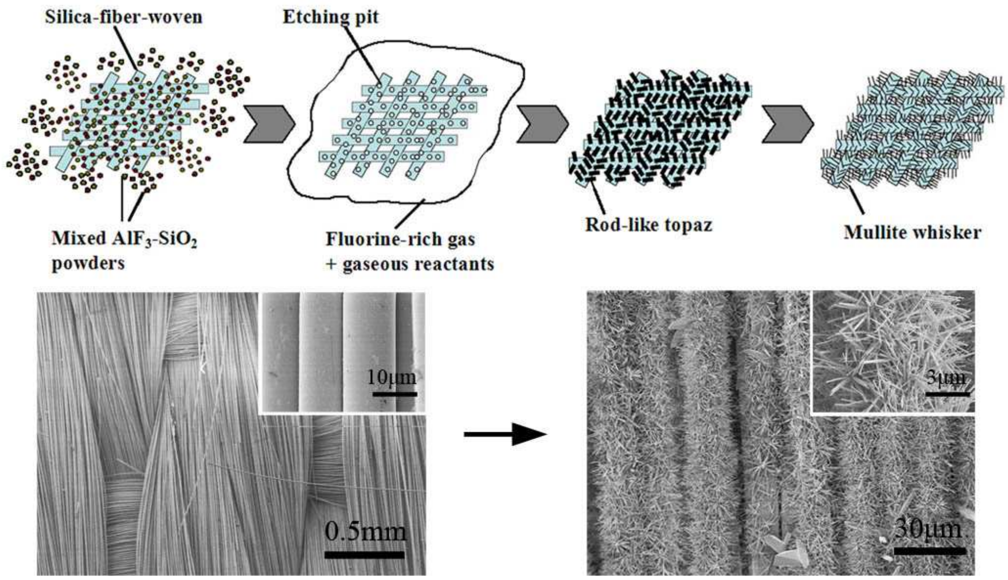
Graphical and textual abstract



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