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Synthesis and properties of lightweight flexible insulant composites with a mullite fiber-based hierarchical heterostructure

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HIGHLIGHTS

- Porous fibrous composites with hierarchical heterostructure were fabricated.
- The secondary structure of nanowhiskers grew uniformly on the mullite fibers.
- The hierarchical structure offered the composites high specific surface area.
- The porosity of the obtained nano-porous composites is high, up to 83.2%.
- Composites possess a low thermal conductivity of 0.132 W/mK and good elasticity.

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ABSTRACT

A novel mullite fibers-based hierarchical heterostructure were fabricated using a sol–gel method. The porous performs were fabricated by mixing the mullite fibers with the aluminum borate xerogel which is derived from the gelation of $Al(OC_4H_9)_3$ and boric acid. After calcination, the preforms with different mole ratio of Al/B, transformed into the composites with hierarchical structures of the aluminum borate nanowhiskers/mullite fiber and alumina plate/aluminum borate nanowhiskers/mullite fiber. The formed aluminum borate nanowhiskers showed a uniform distribution on the mullite fibers, and the growth process may follow a self-catalysis mechanism. The fabricated hierarchical mullite fiber-based products possessed low density of 0.448 g/cm^3, low thermal conductivity of 0.132 W/mK, high specific surface area of 230.7 m^2/g and excellent elastic property with high compression-resilience of 92.7%, and were promising flexible insulant materials for the application in high-temperature heat sealing field.

1. Introduction

In recent years, high temperature sealing problem has received much attentions in the aerospace and energy fields [1,2]. Besides the excellent heat insulation property, the sealing material working in high temperatures must possess a certain degree of elasticity, especially in the application of sealing the joint gap between tow independently movable structural components or the gap between the materials with different thermal expansion coefficients [3–5]. The good elastic property ensures the sealing material could adapt the changes of the sealing gap caused by the movement or the thermal expansion of two different component via the deformation of its own shape, and then could rebound to original state when the system recovered. The most commonly used high temperature sealing material was the ceramic fiber-based porous material, such as ceramic fiber brick with a fixed-point framework. However, the fixed-point structure had a relatively low compression-resilience ratio, which was unfavorable for the sealing effect. In order to further improve the efficiency of the sealing material, one possible solution is to design a component with a new structure.

Hierarchical nanostructures have attracted significant attentions due to their potential applications in the fabrication of nanoelectronics, nanophotonics, energy devices and catalysis [6–9]. Various heterostructures, especially hierarchical meso- and nanoheterostructures, offer unique and useful properties, as they are composed of multiple compositions, controllable sizes, shapes, and morphologies [10–13]. Wang etc. reported the frication of the ZnO/TiO_2 hierarchical structures (ZnO nanostructures growing on the TiO_2 fibers) by a combination of electrospinning and a hydrothermal method [14]. ZnO/WO_x hierarchical heteronanostructures, which have been fabricated using a simple two-step process, have also been reported in the context of a field electron

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emission application [15]. Guo and co-workers reported the preparation of the SiOC fiber/Si_3N_4 nanowires by a two-step process containing the electrospinning and catalyst-assisted pyrolysis method [16]. Nevertheless, complicated experimental procedures and critical conditions, e.g. high temperature, or inert atmosphere were usually required to obtain these fantastic hierarchical materials. Compared with other approaches, sol–gel methods are regarded as an attractive candidate for the synthesis of homogeneous architectures due to the advantages of their environmentally-friendly nature, simplicity, easy controllability and low cost. A wide variety of nanostructures including TiO_2, SiO_2, mullite and Al_2O_3, have been successfully prepared via this method in the past few years [17–20].

Among the inorganic fibers, polycrystalline mullite fiber (which is referred to as PMF in this paper) had been extensively used in high-temperature field, due to its high mechanical strength, low thermal conductivity, high temperature stability, good thermal shock resistance and creep resistance, etc. [21–23]. Our group recently investigated the possibility of the hierarchical structures in the applications of high temperature sealing fields and suggested that the fabricated mullite whisker/fiber composites was a promising sealing material. However, the fabrication of mullite whiskers often involved the toxic AlF_3 atmosphere, which prevented the large-scale production [24].

Another important inorganic fiber, aluminum borate fiber has also aroused great interest due to their stability at high temperature, as a kind of alumina composite, boron-containing alumina materials in an Al_2O_3–B_2O_3 binary system. In this article, we tried to introduce the aluminum borate whiskers, which exhibit excellent physical and mechanical properties as the mullite fiber at high temperature [25,26], into the mullite fiber matrix and investigated their application in heat sealing field.

2. Experiments

Fig. 1 described the synthesis pathway of the composites with hierarchical hetero structure. In our approach, firstly, 6 g of PMF were added into 20 g of mixture of $Al(OC_4H_9)_3$, isopropyl alcohol and ethylacetoacetate (the mole ratio of $Al(OC_4H_9)_3$:isopropyl alcohol: ethylacetoacetate was 1:8:10). After stirring for 1 h, the boric acid was carefully added into the mixture. The mole ratio of $Al(OC_4H_9)_3$ to boric acid was 1:1 and 2:1 (denoted AlB and Al_2B). Then the $Al(OC_4H_9)_3$ would react with the boron acid to form the aluminum borate xerogel which is abbreviated as xerogel in the following manuscript. During the gelation process, the mullite fibers were fixed by the xerogel forming a xerogel/PMF block. The preforms were calcined at 1000 and 1200 °C in air for 2 h. In the calcination process, the aluminum borate xerogel would transform into the aluminum borate nanowhiskers with the mullite fibers as the generation substrate.

Phases of the samples were analyzed via X-ray diffraction (XRD, D/Max-2500 Rigaku, Japan). Microstructure of the sintered samples was observed by scanning electron microscope (SEM, XL-30 Philips, Japan). The specific surface areas were measured by an automatic mercury injection apparatus (IV9500, Micromeritics Instrument Corporation, USA). The densities were calculated by the following equation: $\rho = m/v$, where m and v were the weight and the volume of the sample after sintered, respectively. Porosities of the sintered samples were determined by Archimedes method namely the water-immersion technique with the following equation: $P = [(m_2 - m_0)/(m_2 - m_1)] \times 100\%$, where m_2 is the weight of the sample after the pores of the sample is full filled with water, m_0 and m_1 are weight of the sample immerse in air and water, respectively. Thermal conductivity at room temperature was measured by the thermal-conductivity instrument (C-3000, Xian Xiaxi Electric Co., Ltd., Shanxi, China). The average linear thermal expansion coefficients were obtained from the temperature dependent changes of the length of the specimen from room temperature to 1200 °C in air by using a high-temperature dilatometer (Setaram Setsys 24, Caluire, France). Compression-rebound tests were carried out at room temperature on an electro-universal testing machine (Instron 5569, USA) in accordance with GB/T 1964–1996. During the test a set of loads were applied to the samples at a loading speed of 0.05 mm/min, and removed at an unloading speed of 0.05 mm/min. The compressive ratio and resilience ratio were determined by the following equations: compressive ratio = $[(t_0 - t_1)/t_0] \times 100\%$, resilience ratio = $[(t_2 - t_1)/(t_0 - t_1)] \times 100\%$, where t_0 is the thickness of the sample before loading, t_1 is the thickness of the sample during loading, and t_2 is the thickness of the sample after unloading. The dimensions of measured samples were 30 mm in diameter and 10 mm in thickness. Each value represented an average of five measurements of five different specimens.

3. Results and discussion

According to the phase diagram of Al_2O_3–B_2O_3, there are only two stable compounds at the ambient pressure, namely $Al_4B_2O_9$ and $Al_{18}B_4O_{33}$ [27,28]. The former is found to be thermally stable below 1000 °C, and to decompose into $Al_{18}B_4O_{33}$ and boron oxide vapors at a temperature higher than 1000 °C.

In order to study the thermal behavior and structure modification by calcination temperature and reactant composition, TG–DTA and XRD tests for the starting materials were carried out at an air atmosphere. All products showed similar thermal behavior. Fig. 2A showed the TG–DTA curves of PMF and AlB xerogel, respectively. As to the system of PMF, the weight loss of ~0.3% up to ~1200 °C associated with a very broad exothermal peak was related to the evaporation of the polymer on the surface of the mullite fiber. For the system of AlB xerogel, the weight loss of ~70% up to ~450 °C associated with several endothermal peaks was attributed to the decomposition of H_3BO_3 and $Al(OH)_3$, and the melting of boron oxide. When the reaction temperature was higher than 1000 °C, the evaporation of boron oxide occurred

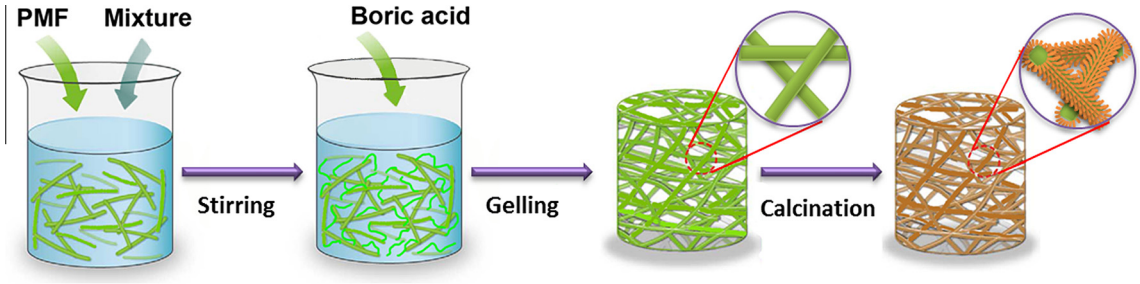

Fig. 1. Synthesis steps of the composites with hierarchical heterostructure.