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Ultra-low thermal conductivity and high strength of aerogels/fibrous ceramic composites

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ABSTRACT

Novel aerogels/fibrous ceramic composite, inspired by the bird's nest structure in nature, is synthesized using mullite fibers as matrix and ZrO_2–SiO_2 aerogels as filler through vacuum impregnation. Thus, the macropore of mullite fiber perform are filled by aerogels to form similar bird's nest structure with high porosity (85%) with a large amount of mesoporous. The as-prepared aerogels/fibrous ceramic composite exhibits high compressive strength of up to 1.05 MPa which is approximately two times as much as that of mullite fiber perform and ten times higher than that of pure aerogels, and the compressive failure mechanism is analyzed. Compared to conventional fibrous materials, the aerogels/fibrous ceramic composite shows a much lower thermal conductivity of 0.0524 W m^{-1} K^{-1} at room temperature and 0.082–0.182 W m^{-1} K^{-1} during 500 °C and 1200 °C indicating its excellent thermal insulation property in a wide temperature range. Therefore, this ultra-low thermal conductivity aerogels/fibrous ceramic composite with high strength is an excellent heat-insulation material applied in the fields of aerospace.

1. Introduction

Recently, high thermal protection problem has received much attention in the fields of aerospace and energy fields [1,2]. In order to satisfied the most stringent requirements due to severe thermal and mechanical service environments such as atmospheric reentry missions, the thermal protection materials must possess low density, high strength and excellent heat-insulating property especially at high temperature [3,4].

The concept of using low-density fibrous materials for advanced aerospace vehicles was introduced by the Lockheed Missiles and Space Company in 1962 [5]. The design criteria compromises of fibrous materials were focus on strength and density, because advanced lifting reentry vehicle concepts needed the low weight and rigid heat shields [6]. Recently, a novel structure of fibrous material was fabricated by Dong et al. [7–9] using mullite fibers as matrix and silica–boron sols as high temperature binder. It was reported that this fibrous material exhibits good elasticity performance, relatively high strength and high porosity. However, this fibrous material showed a high thermal conductivity with 0.231 W m^{-1} K^{-1} because the solid thermal conduction of fibers and the convection thermal transfer of gas in the fiber-lap hole, which limited the application of fibrous materials.

Interestingly, it can be found that the bird's nest is a natural highly porous fiber network material, which is made of randomly arranged tree branches with a three-dimensional structure. In order to improve insulation of their nest, some wise birds add an insulation layer in the nest. For instance, Spotted Thrush's nest is made of tree branches as skeleton and animal wools as filler [10]. Animal wools are introduced to fill the nest because they exhibit a low thermal conductivity with 0.055 W m^{-1} K^{-1} [11] and they can be used to eliminate the gas or decrease the pore size to be less than the mean free path of air in the branch-lap hole. Therefore, the nest shows an excellent heat-insulating property. Inspired by this unique bird's nest structure, the idea of decreasing the thermal conductivity of fibrous material by adding light-weight thermal insulation materials as filler is brought.

Aerogels are highly mesoporous solid materials with extremely low density, high porosity and specific surface areas [12–15]. The pore size of aerogels is less than the mean free path of air (0.13 μm), which is useful to decrease the collision frequency of air molecules. Thus, this unique structure of aerogels results in low thermal conductivity. Meanwhile, ZrO_2–SiO_2 aerogels exhibit a higher specific surface area (~228 m^2/g) after 1000 °C calcination, which is higher than that of pure aerogels (~82 m^2/g) [16]. Thus, ZrO_2–SiO_2 aerogels show a more stable property at 1000 °C than that of pure

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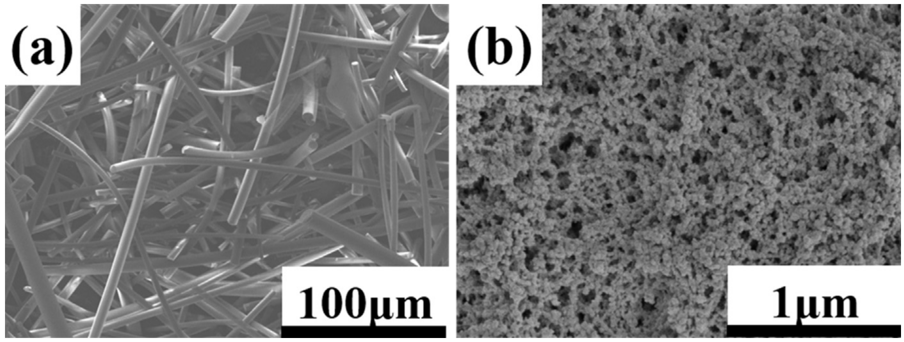

Fig. 1. SEM image of (a) mullite fiber and (b) ZrO_2–SiO_2 aerogel.

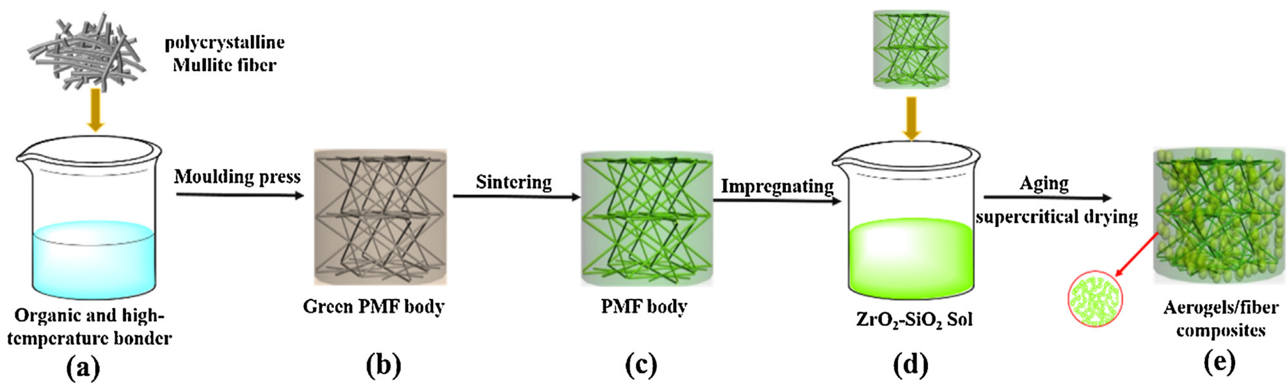

Fig. 2. Prepare processing of aerogels/fibrous ceramic composites (AFC).

aerogels because zirconia exhibits high temperature resistance and the unformed silica restrains the phase transition of zirconium. Polycrystalline mullite fiber (PMF) is an attractive material applied in high temperature in oxidizing environment because of the combination of high thermal stability, high mechanical strength, good chemical stability and creep resistance [17–20]. In our study, imitating the unique bird's nest structure, the novel fibrous material is prepared by PMF as skeleton and ZrO_2–SiO_2 aerogels as filler. The aerogels/fibrous ceramic composite (AFC) exhibits high strength and high porosity. Moreover, AFC shows an ultra-low thermal conductivity because the fiber-lap holes are filled by mesoporous aerogels with low thermal conductivity.

2. Experimental

2.1. Raw materials

Commerically available polycrystalline mullite refractory fibers (PMF, 99.5%, Zhejiang Hongda Crystal Fiber Co., Ltd., China) were used as starting materials. The organic bind (OB) was prepared by mixing sodium dodecyl benzene sulfonate (SDBS) and polyacrylamide (CPAM) in distilled water with weight ratios SDBS: CPAM: H_2O = 1:1:100. The high temperature binder was composed of silica sol and boron nitride (BN AR grade, Tianjin Jiangtian Chemical Co., China), with a weight ratio Si: B = 10:1. The silica sol was produced with tetraethylorthosilicate (TEOS, AR grade, Tianjin Jiangtian Chemical Co., China) as precursor by one-step catalytic method and the molar ratio was TEOS: H_2O: ethanol: nitric acid = 1: 4: 6: 0.8. ZrO_2–SiO_2 composite aerogel was prepared with TEOS and $ZrOCl_2$ (AR grade, Tianjin Jiangtian Chemical Co., China) as precursor by prehydrolysis [21–23]. 1,2-epoxyporopane (Po, AR grade, Tianjin Guangfu Chemical Co., China) was used as gelation promoter to ensure the rapid gelatin of sol. Nitric acid (HNO_3, AR grade, Tianjin Kemiou Chemical Co., China) was used as catalyst. Polyethylene glycol 600 (PEG, AR grade, Tianjin Guangfu Chemical Co., China) and formamide (FA, AR grade, Tianjin Guangfu Chemical Co., China) were respectively used as dispersant and dry control chemical agent.

Fig. 1(a) shows the micrograph of the mullite fibers which possess a diameter in the range of 10–15 μm and a length in the range of 200–400 μm. Fig. 1(b) presents the micrograph of the ZrO_2–SiO_2 composite aerogels which possess a three-dimensional network constructed by homogeneous and elliptic gel particles.

2.2. Experimental procedure

Fig. 2 shows the processing steps of AFC and the schematic diagram of the structure of the AFC. First, PMF (6 g), the organic binder (30 g) and the high-temperature binder (1 g) were mixed together by stirring (Fig. 2(a)). The fibers formed into a fiber block with the help of a certain amount of organic binder coated on the fiber surface by mould pressing (Fig. 2(b)). Then, the PMF perform was obtained by sintering at 1200 °C for 15 min (Fig. 2(c)). It could be found that the PMF was linked together at the crossing points with the help of high-temperature binder melting into continuous phase. Whereafter, the PMF prefabricated body was impregnated into ZrO_2–SiO_2 composite sols under vacuum. After aging, alcohol-water exchanging and supercritical drying [24,25], the AFC was synthesized (Fig. 2(e)). The most important structure of AFC was that the mullite fibers constituted a special 3-D skeleton structure, and the fiber-lap hole was filled by the aerogels with a large amount of mesoporous.

2.3. Characterization

Microstructure of the samples was observed by scanning electron microscope (SEM, XL-30Philips, Japan). The nitrogen adsorption and desorption isotherms at 77 K were measured using