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Enhanced mechanical and thermal properties of anisotropic fibrous porous mullite–zirconia composites produced using sol-gel impregnation

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ABSTRACT

A new lightweight and thermal insulating material was successfully prepared by impregnating Al_2O_3–SiO_2 aerogel into a porous mullite–zirconia fiber network with a quasi-layered microstructure. The microstructures, thermal and mechanical properties of the porous mullite–zirconia ceramics were investigated before and after the impregnating of Al_2O_3–SiO_2 aerogel. It was observed that the mullite and zirconia fibers combined well with aerogels. Compared with fibrous porous mullite-zirconia ceramics, the Al_2O_3–SiO_2 aerogel/porous mullite–zirconia composite exhibited higher compressive strength (i.e. 1.36 MPa in the *z* direction) and lower thermal conductivity (i.e. 0.052 W/(m·K)). The present work provides an efficient way to fabricate highly porous ceramics with high strength and ultra-low thermal conductivity, which find potential use in high-temperature thermal insulation materials.

1. Introduction

Highly porous ceramics are widely used in applications such as fuel-cell electrodes, molten metal filtration, catalyst supports and high-temperature thermal insulation [1–4]. Usually, mechanical stability must be combined with at least one other functional property such as a low dielectric constant, high permeability, or low thermal conductivity. For example, for bulk thermal insulation used in the aerospace industry, porous ceramics need to have low density, low thermal conductivity, and high melting point and strength. Recently, many porous ceramics with low thermal conductivity and relatively high strength have been prepared using different methods, such as gel casting, adding fugitive substances, and freeze casting [5–7]. Hu et al. [5] prepared porous zirconia ceramics by TBA-based gelcasting process, and the sample with high porosity of 52–76% and low thermal conductivity of 0.06–0.42 W/(m·K) was achieved. Schlichting et al. [6] fabricated porous zirconia ceramics using fugitive polymer method and studied the thermal conductivity. Porous rare-earth silicate ternary ceramics, including $Y_2Si_2O_7$, Y_2SiO_5, $Yb_2Si_2O_7$, and Yb_2SiO_5, have recently attracted considerable attention for use as an ultra-high-temperature thermal insulation material because of their superior high-temperature stability, low thermal conductivity, and excellent hot-corrosion resistance [8–12]. Porous Y_2SiO_5 ceramics with relatively high compressive strength (23.2 MPa) and ultra-low thermal conductivity (0.10 W/m·K) were fabricated by using a TBA-based freeze casting method [9]. In our previous study [10–12], porous Yb_2SiO_5 ceramics prepared using a water-based freeze casting method exhibited high porosity (i.e. 79.1%), high compressive strength (i.e. 4.9 MPa), low dielectric constant (i.e. 2.38) and low thermal conductivity (i.e. 0.168 W/(m·K)) [10]. However, these works were devoted to the fabrication of porous ceramics using powder as a raw material; therefore, these materials exhibited low mechanical reliability and are not suitable for aerospace vehicles.

In order to obtain an increase in mechanical reliability, a porous fiber network with a bird's nest structure was prepared using vacuum moulding. Compared with gel-casting or freeze-casting methods, vacuum moulding has attracted more attention as a simple, versatile, and low-cost fabrication method for porous ceramics. The resulting fibrous porous ceramics with ultra-low thermal conductivity and high tolerance to damage can be attributed to the fibrous structure of the material as the fibers are only bonded at crossing points. Fibrous porous mullite ceramics with low densities (0.560–0.595 g/cm^3) were prepared by Dong et al. [13] and had low

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thermal conductivity (0.157–0.165 W/m·K), relatively high compressive strength (1.1–2.1 MPa), and high rebound-resilience (77%–90%). Sun et al. [14] fabricated porous fibrous zirconia ceramics with a high porosity (72%–89%), a low thermal conductivity (0.056–0.16 W/(m·K)), and a relatively high compressive strength (0.6–13.3 MPa). However, the density of porous zirconia fiber networks was relatively high (0.67–1.72 g/cm^3).

In our previous work, we propose a new vacuum squeeze moulding method for preparing lightweight porous mullite–zirconia fiber networks with a quasi-layered microstructure [15]. The low zirconia fiber content of porous fiber networks is actually one reason why the thermal conductivity of fibrous porous ceramics was slightly decreased. Therefore, porous mullite–zirconia fiber networks with high zirconia fiber content were prepared by vacuum squeeze moulding in this study. Moreover, Al_2O_3–SiO_2 aerogels are highly mesoporous solid materials with high-temperature stability, ultra-low thermal conductivity and density [16]. In order to obtain higher compressive strength and lower thermal conductivity of fibrous porous ceramics, the porous mullite–zirconia fiber networks are filled by Al_2O_3-SiO_2 aerogels to form aerogels/fibrous ceramic composite. The microstructure, thermal and mechanical properties of porous fibrous porous mullite-zirconia ceramics were investigated before and after the impregnation of Al_2O_3–SiO_2 aerogel. As far as we know, a few studies [17] have been reported concerning the heat transfer characteristics of porous fibrous ceramics at high temperature. Hence, the heat transfer characteristics inside porous materials at high temperatures were also analyzed in this study.

2. Experimental procedures

Polycrystalline mullite refractory fiber (PMF, 99.5%, Zhejiang Hongda Crystal Fiber Co., Ltd., China) and zirconia fiber (8mol.% Y_2O_3–ZrO_2, Anhui Crystal New Materials Co. Ltd., China) was used as the raw material of the skeleton structure. The mullite fiber had a diameter of 3–5 μm and a length of 300–500 μm; the ZrO_2 fiber had a diameter of 4–7 μm and a length of 300–500 μm. The fabrication flow chart of the mullite fibrous ceramics is shown in Fig. 1. The mix slurries in this work were prepared by adding mullite and zirconia fibers into the distilled water. And then 0.5 wt% polyacrylamide dispersant (Sigma-Aldrich Trading Co., Ltd., China), 5 wt% starch binder (Sinopharm Chemical Reagent Co. Ltd., China), 7.5 wt% SiC sintering aids (purity > 99.5%, particle size ~0.5 μm, Weifang Kaihua Micro-powder Co. Ltd., China), 7.5 wt% B_4C sintering aids (purity > 98.1%, particle size ~1 μm, Jingangzuan Boron Carbide Co. Ltd., China) and 5 wt% polyethyleneimine adsorbent (Sigma-Aldrich Trading Co., Ltd., China) were added into the premix solution with continuous stirring. Then the slurry was vacuum squeeze moulded to remove excess water and to form a soft felt. In order to determine the optimum process parameters, the effects of initial pressure (20 KPa–80 KPa) and ZrO_2 fiber contents (20 vol %-60 vol%) on the microstructure and properties of the fibrous porous mullite–zirconia ceramics were investigated. After drying in an oven at 80–100 °C for 24–28 h, the dried felt was sintered at 1400 °C for 1 h in air, with a heating rate of 3 °C/min. Finally, the sintered samples were machined to the required shape and size.

In this experiment, Al_2O_3–SiO_2 sols were synthesized using aluminum chloride hexahydrate ($AlCl_3 \cdot 6H_2O$) and tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) as precursors, ethanol (EtOH) as a solvent, and propylene epoxide (PO) as a catalyst. The sols were prepared according to the following steps: $AlCl_3 \cdot 6H_2O$, TEOS, EtOH, and H_2O were directly mixed in a pot with a molar ratio of 1:0.33:15:50, stirred for approximately 2 h at 50 °C for complete hydrolysis, and then cooled to room temperature. PO was added with vigorous stirring. After stirring for 30 min, the porous mullite–zirconia fiber network was impregnated with the Al_2O_3–SiO_2 sol under vacuum. Wet gel was formed in the porous network of the porous mullite–zirconia ceramics by aging for 48 h at room temperature. The gel parts were subsequently soaked in a bath of absolute ethanol for 4 days to exchange the water (Fig. 1). Finally, supercritical drying was performed (the critical point is $T_c = 270$ °C and $P_c = 10$ MPa for ethanol) to obtain non-cracked porous ceramic–aerogel composites.

The microstructure of the composites was observed by the scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, USA). The bulk density was calculated based on the sample's weight and the corresponding volume. Porosity was calculated from the ratio of apparent density of porous samples to the theoretical density of dense ceramic. Each parameter was an average of the results of at least five samples. The pore size distribution of Al_2O_3-SiO_2 aerogels were measured by Nitrogen adsorption experiments performed on an Autosorb-1 instrument (Quantachrome, Inc.). The determination of the thermal conductivity was measured by the thermal-conductivity instrument (DRE-III, Xiangtan Xiangyi Instrument Co., Ltd., Xiangtan, China). The compressive strength of the cylindrical samples with Φ 15 mm × 20 mm was measured by a testing machine (Zwick Z050, Zwick, Ulm, Germany) with a crosshead speed of 1.0 mm/min. The samples were machined with the compressive surface perpendicular to the pressing direction. More than six samples of each measurement were selected to obtain the average value.

3. Results and discussion

Fig. 2 shows the SEM images of the fiber skeleton structure fabricated using different ZrO_2 fiber contents. As shown in Fig. 2(a), the morphology of the skeleton structure showed a network of interconnected polycrystalline mullite and zirconia fibers. Moreover, the mixed B_4C and SiC melted into the borosilicate glass phase during sintering in air and only bonded the fibers well at the

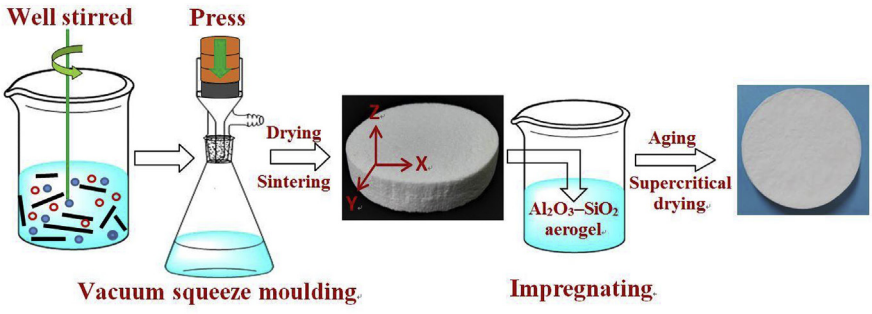

Fig. 1. Fabrication flow chart of Al_2O_3–SiO_2 aerogel/porous mullite-zirconia composites.