Materials Letters 175 (2016) 219–222

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

A novel silica aerogel/porous Y_2SiO_5 ceramics with low thermal conductivity and enhanced mechanical properties prepared by freeze casting and impregnation

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ARTICLE INFO

Article history:
Received 1 February 2016
Received in revised form
28 March 2016
Accepted 5 April 2016
Available online 7 April 2016

Keywords:
Porous materials
Freeze casting
Ultra-high porosity
Thermal properties

ABSTRACT

A novel silica aerogel/porous Y_2SiO_5 composite was prepared by freeze casting and sol-gel impregnation. Porous Y_2SiO_5 ceramics with different solids contents were prepared at 1400 °C. The pore structure, porosity and mechanical properties of the porous Y_2SiO_5 ceramics before and after impregnating of silica aerogel were investigated. The results show that the room-temperature thermal conductivity decreases and the compressive strength increases remarkably while impregnating porous Y_2SiO_5 with silica aerogel. The silica aerogel/porous Y_2SiO_5 composite exhibits a high compressive strength (i.e. 9.3 MPa) and a low thermal conductivity (i.e. 0.260 W/(mK)). This work reports an optimal processing method of silica aerogel/porous Y_2SiO_5 composite with the potential application as a high-temperature thermal insulation material.

1. Introduction

The high melting points of Rare-earth silicates (RE-Si-O oxides), including $Y_2Si_2O_7$, Y_2SiO_5, $Yb_2Si_2O_7$ and Yb_2SiO_5, have recently attracted considerable attention because of their superior high-temperature stability, low thermal conductivity and excellent hot-corrosion resistance [1–3]. Recently, porous RE-Si-O ternary ceramic has been widely studied as a novel high-temperature thermal insulator material because of their low density, low thermal conductivity, high melting point and strength [4–9]. Porous RE-Si-O ternary ceramics were prepared using different methods, such as adding fugitive substance, foam-gelcasting, *tert*-butyl alcohol (TBA) based gel-casting and TBA-based freeze casting [4–7]. Wang et al. [4] fabricated reticulated porous γ-$Y_2Si_2O_7$ ceramics with high porosity (~85%) and relatively high compressive strength (~1.28 MPa) by the polymeric sponge impregnation method. Single-phase porous γ-$Y_2Si_2O_7$ ceramic was fabricated by foam-gelcasting and in-situ reaction sintering method, and the sample sintered at 1550 °C has low linear shrinkage (6.0%), high porosity (84.9%), high compressive strength (6.22 MPa), and low thermal conductivity (0.230 W/(m K)) [5]. Liu et al. [6] prepared porous Y_2SiO_5 ceramics by TBA-based gel-casting, which had an open porosity of 61.80%, a low room-temperature thermal conductivity of 0.17 W/m K and a relatively high compressive strength of 13.91 MPa. Li et al. [7] fabricated porous Y_2SiO_5 ceramics with relatively high compressive strength (as high as 23.2 MPa) and ultra-low thermal conductivity (approximately 0.10 W/m K) using a TBA-based freeze casting method.

Recently, we proposed a water-based freeze-casting method to prepare highly porous Y_2SiO_5 and Yb_2SiO_5 ceramics [8–11]. Compared with TBA- or camphene-based freeze-casting, water-based freeze-casting has attracted more attention as a simple, versatile, low-cost, and environmentally friendly fabrication method for porous ceramics. In the previous study, as the solids content was increased from 10 to 25 vol%, the compressive strength of the porous Y_2SiO_5 ceramics increased from 1.87 to 8.42 MPa [8], and the compressive strength and thermal conductivity of the porous Yb_2SiO_5 ceramics increased from 2.82 to 7.01 MPa and 0.113–0.301 W/(mK), respectively [10]. However, these performances are not enough to making them enough suitable for high-temperature thermal insulation application.

In the current study, in order to obtain higher compressive strength and lower thermal conductivity of porous Y_2SiO_5 ceramics, we prepared silica aerogel/porous Y_2SiO_5 composite by freeze-casting and sol-impregnating. The pore structure, porosity and mechanical properties of porous Y_2SiO_5 ceramics before and

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http://dx.doi.org/10.1016/j.matlet.2016.04.051
0167-577X/

after impregnating of silica aerogel were investigated. We expect the results of this study to promote porous Y_2SiO_5 ceramics as good candidates for ultra-high temperature thermal insulator materials.

2. Experimental procedures

Highly porous Yb_2SiO_5 ceramics with different solid contents (10–25 vol%) were fabricated by freeze-casting and sintering. The detailed freeze-casting process can be found in our previous work [10]. The green compacts were carefully placed into a ZrO_2 crucible and sintered in a convection furnace under air atmosphere at 1400 °C for 60 min. Both the heating and cooling rates were 5 °C/min.

In this experiment, additionally, tetraethoxysilane (TEOS), ethanol (EtOH) and water were mixed together with a molar ratio of 1:7:4 as precursors for the silica. The pH value of the above mixture was adjusted to 2 by addition of hydrochloric acid (HCl). The TEOS/EtOH/HCl/H_2O mixture was refluxed at 80 °C for 40 min. And then, 0.25 ml of 0.05 mol $NH_3 \cdot H_2O$ was added to the solution and mixed for about 10 min until solution became transparent. After stirring for 30 min, the porous Y_2SiO_5 ceramic was impregnated with the silica sol under ultrasonic vibration. Wet gel formed in the porous network of the porous Y_2SiO_5 by aging in TEOS/EtOH solution for 48 h, the pore fluids in the wet gel were exchanged with ethanol to facilitate subsequent surface modification. Finally, supercritical drying was performed (i.e. the critical point is Tc=260 °C, Pc=9.3 MPa for ethanol) to acquire non-cracked porous ceramic–aerogel composites.

The bulk density of porous Y_2SiO_5 ceramic before and after impregnating of silica aerogel was measured from the sample mass and dimension, and the relative density, and thus the porosity, was determined from the ratio of the measured bulk density to the theoretical density of Y_2SiO_5 ceramic [12]. Each parameter was an average of the results of at least five samples. The pore size distributions were analyzed by a mercury intrusion porosimetry (AutoPore 9500, Micromeritics Instrument Corp., United States). Thermal conductivity was measured by the guarded heat flow test method (DRE-III, Xiangtan Xiangyi Instrument Co., Ltd., Xiangtan, China). According to GB/T 8489-2006 standard [13], the compressive strength of the cylindrical samples with Φ(11–14) mm × 20 mm was measured by a testing machine (Zwick Z050, Zwick, Ulm, Germany) with a crosshead speed of 0.5 mm/min. The samples were machined with the compressive surface perpendicular to the freezing direction. More than six samples of each measurement were selected to obtain the average value. The microstructure of the as-prepared products coated with a thin layer of gold was observed by a scanning electron microscope (FEI Quanta 200, FEI Company, Hillsboro, USA).

3. Results and discussion

The total porosity is controlled, as a first-order parameter, by the initial solid loading of the suspension [14]. Table 1 showed the porosities of porous Y_2SiO_5 ceramic before and after impregnating of silica aerogel. As showed in Table 1, the initial solids content was observed to influence the porosity, when the initial solids content was increased from 10 to 25 vol%, the porosity of initial porous Y_2SiO_5 ceramics prepared at 1400 °C decreased from 88.4% to 73.3%. After impregnating of silica aerogel, the porosity of porous Y_2SiO_5 ceramic prepared at 1400 °C decreased from 86.4% to 71.3%, which was higher than that before impregnation at the corresponding initial solids content. The porosity of porous Y_2SiO_5 ceramics after impregnating of silica aerogel increased slightly, because the porous Y_2SiO_5 ceramics prepared by freeze-casting in liquid nitrogen bath, the surface layer of the porous ceramic was relatively dense, and the impregnating capacity of silica aerogel was limited.

Fig. 1a–d show the morphology of porous Y_2SiO_5 ceramics with different solids content prepared at 1400 °C. As showed in Fig. 1, the pores evolved from dendritic to three-dimensional reticular shapes as the solids content was increased from 10 to 25 vol%. The similar conclusion was obtained in our previous study [10]. When the solid loading was less than 20 vol% (Fig. 1a–b), the pore channel size of the sample decreased as the solids content was increased. Because the solid particles at the solidification fronts were more effectively rejected, the unidirectionally aligned channels were more easily formed along the thermal gradient direction. As the solids content was increased to 25 vol%, the solid particles at the solidification fronts were effectively engulfed, and turned to form reticular pore walls (Fig. 1c). Moreover, the pore size distribution curves of the samples present a single peak with a narrow width (Fig. 1d), signifying uniform pore size distributions. The mean pore size generally decreased from 18.2 ± 1.8 to 12.1 ± 1.1 μm with increasing the solids content from 10 vol% to 25 vol%, which means that the pore size is sensitive to the solids content.

The microstructure of the porous Y_2SiO_5 ceramics after impregnation with silica aerogel was observed in Fig. 2. Silica aerogel obviously occupied most places of the pore channels of porous Y_2SiO_5 ceramics (Fig. 2a-b). As the solid loading was less than 20 vol%, as shown above, the unidirectionally aligned channels were formed in the porous ceramic, the silica aerogel easily impregnating into the porous ceramic, and the surface of silica aerogel/porous Y_2SiO_5 ceramics was relatively smooth. However, when the solids content was increased to 25 vol%, the surface of porous Y_2SiO_5 ceramics with reticular pore was relatively dense, the impregnating capacity of silica aerogel was limited, and so the surface of silica aerogel/porous Y_2SiO_5 ceramics became wavy. Fig. 2(c)-(d) showed the corresponding enlarged micrographs of silica aerogels formed in the pore structure. The silica aerogel consists of nanoparticles and nanopores, spherical SiO_2 particles a few tens of nanometers in size form a 3-D network containing homogeneous nanopores (size in the range of 50–80 nm).

Table 1 also shows the compressive strength of porous Y_2SiO_5 ceramics before and after impregnating of silica aerogel. As the solids content was increased from 10 to 25 vol%, the compressive strength of porous Y_2SiO_5 ceramics before and after impregnating

Table 1
Porosity, thermal conductivity, and compressive strength of porous Y_2SiO_5 ceramics before and after impregnation with silica aerogel.

Solid content (vol%)	Porosity[b] (%)	Thermal conductivity[b] (W/m K)	Compressive strength[b] (MPa)	Porosity[a] (%)	Thermal conductivity[a] (W/m K)	Compressive strength[a] (MPa)
10	88.4	0.079 ± 0.002	0.5 ± 0.07	86.4	0.069 ± 0.004	0.9 ± 0.3
15	83.9	0.148 ± 0.006	1.6 ± 0.13	81.7	0.115 ± 0.002	2.4 ± 0.2
20	79.8	0.178 ± 0.005	2.1 ± 0.20	77.7	0.141 ± 0.004	3.2 ± 0.5
25	73.3	0.286 ± 0.010	5.1 ± 0.15	71.1	0.260 ± 0.006	9.3 ± 0.3

The superscripts a and b denote values after and before impregnation with aerogels, respectively.