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One-step synthesis of monolithic micro-nano yttria stabilized ZrO_2-Al_2O_3 composite aerogel

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ABSTRACT

Monolithic micro-nano yttria-stabilized ZrO_2 (YSZ)-Al_2O_3 composite aerogel composed of Al_2O_3 hollow microspheres which was filled with YSZ nanoparticles was prepared by one-step sol-gel process. Such aerogel-like microstructure combined the advantages of good high temperature tolerant property of Al_2O_3 hollow microspheres and favorable thermal insulation property of porous YSZ aerogel, while the mechanical strength of the structure also significantly increased. The micro size voids in the Al_2O_3 hollow microspheres were filled by YSZ aerogels thus resulted in more mesopores which contributed to block heat transfer up to 1200 °C. By optimizing the ratio of YSZ in the composite, the obtained composite aerogel showed good thermal stability (linear shrinkage = 9.7%), low room temperature thermal conductivity (0.032 W/mK) and high elastic moduli (3.47 MPa) after 1200 °C heat treatment.

1. Introduction

Metal oxide aerogels have been considered as excellent thermal insulation materials [1]. From the view of the pathways of heat transfer, the characteristics such as high porosity, low solid density, small particle size (below 10 nm), as well as developed pore structure (mainly below 100 nm) in aerogel could effectively block the heat transfer through both solid and gas phase [1–5]. However, previous literature showed that metal oxide aerogels subjected to several microstructure degradations at high temperatures. For examples, SiO_2 aerogel can only work below 650 °C [6]. Al_2O_3 aerogels [7] displayed significant shrinkage and lost their mesoporous microstructure after high temperature (>1000 °C) heat treatment, due to the severe sintering process caused by the high surface free energy of nano particles. As for ZrO_2 aerogel, it has been reported [8,9] that the surface area decreased significantly after 800 °C heat treatment and the mesoporous microstructure collapsed thoroughly. One of possible reasons for the poorer thermal stability of ZrO_2 aerogel is the stress caused by the phase transformation at high temperatures [10]. Such stability issues hinder the further application of metal oxide aerogels in TPS (thermal protection system) for aerospace vehicles [11].

In response to the above drawbacks, many efforts have been devoted on improving the stability of metal oxide aerogels at high temperatures. One possible route is to modify the microstructure and composition of aerogel during synthesis. For instance, Al_2O_3 aerogels modified by liquid deposition can maintain their mesoporous structures at 1300 °C [12]. Core-shell nanostructured ZrO_2 aerogels prepared by immersing wet gel in silica colloidal solution can tolerate 1000 °C heat treatment [12]. In the meantime, aging ZrO_2 gel in tetraethyl orthosilicate (TEOS) solution is an effective way to obtain crack-free aerogel [13–15]. SiO_2 from partially hydrolyzed TEOS could enhance the connection between the nanoparticles, thus the mechanical property of the aerogel can be improved. Yttria has also been adopted to stabilize the crystalline phase of zirconia. Yttria-stabilized ZrO_2 (YSZ) aerogel maintains cubic phase from room temperature to 1200 °C which avoided the possible phase transformation compared with un-stabilized ZrO_2 [16,17].

On the other hand, several types of aerogel-like metal oxide monolith have been reported very recently. Especially, monolithic aerogel-like alumina with high temperature stability has been proposed by Wu et al. [18]. Such material was prepared by the

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accumulation of mesoporous Al_2O_3 hollow microspheres, and exhibited the same characteristics comparable to aerogel, such as low bulk density (0.133 g/cm^3), high surface area (505.6 m^2/g) and high porosity. Unlike traditional aerogel, which is composed of connected nanoparticles (3–5 nm), the subunits in such material are replaced by sub-micro size Al_2O_3 hollow spheres. Moreover, excellent thermal stability of the aerogel-like alumina (8% linear shrinkage at 1200 °C) was found. However, the room temperature thermal conductivity (eg. 0.036 W/(mK)) of this material is significantly higher than that of its aerogel counterpart. This is due to the presence of the micro size voids in the hollow microspheres which could not entrap the air molecule from free collision or convection, thus the heat transfer through gas cannot be effectively blocked [1].

It is then reasonable to further modify the aerogel-like alumina by filling the hollow microspheres with other metal oxide aerogel, which will bring more mesopores (20–50 nm) to block the heat transfer through gas. In the meantime, the advantages of good thermal stability of such aerogel-like materials should be reserved. In this paper, we rationally filled the micro size voids with yttria-stabilized zirconia (YSZ) aerogel to form a new type of micro-nano YSZ-Al_2O_3 composite aerogel. The as-prepared YSZ-Al_2O_3 composite aerogel composed of YSZ aerogels filled Al_2O_3 hollow microspheres has lower room temperature thermal conductivity (0.026 W/mK), high mechanical strength and maintains good thermal stability after 1200 °C heat treatment.

2. Experimental

2.1. Synthesis

Polyethylene oxide (PEO) was used as soft template. Aluminum chloride hexahydrate ($AlCl_3{\cdot}6H_2O$) and zirconium oxychloride octahydrate ($ZrOCl_2{\cdot}8H_2O$) were used as aluminum and zirconium sources. Yttrium nitrate hexahydrate ($Y(NO_3)_3{\cdot}6H_2O$) was used as zirconia stabilizer. Formamide (FA) and polyethylene glycol 600 (PEG600) were used as control chemical agent and dry dispersant, respectively. Propylene epoxide (PO) was added as gelation agent. The above chemical agents were obtained from Sinopharm Chemical Reagent Corporation (China).

The wet gel was prepared with the starting compositions listed in Table 1. Firstly, 0.549 g of PEO was dissolved in a mixture of ethanol and distilled water and stirring vigorously for 2 h. After the formation of transparent solution, 19.5 g of $AlCl_3{\cdot}6H_2O$, proper amount of $ZrOCl_2{\cdot}8H_2O$ and $Y(NO_3)_3{\cdot}6H_2O$ were added and stirring was continued for 1 h. Then, FA and PEG600 were added to form homogeneous solution. After stirring for 15 min, proper amount of PO was poured into the solvent under 35 °C and stirring vigorously for 1 min. The wet gel would form in 5 min and then it was maintained at 40 °C to complete gelation. The samples were denoted as ZA-0, ZA-1, ZA-2 and ZA-3 according to the molar ratio of ZrO_2:Al_2O_3 (ZA-0: n (ZrO_2) = 0, ZA-1: n (ZrO_2):n (Al_2O_3) = 1:5, ZA-2: n (ZrO_2):n (Al_2O_3) = 1:2.5 and ZA-3: n (ZrO_2): n (Al_2O_3) = 1:1.25).

After gelation, the wet gel was aged in isopropanol for 1 day at 40 °C. The wet gel was then soaked in a bath of isopropanol/TEOS solution (1:1 in volume) for 3 days. Finally, the excessive soluble impurity in the wet gel was washed with isopropanol for several times. Then the aged gels were transferred into an autoclave and dried in supercritical ethanol. The final temperature and pressure of the system were 260 °C and 7.5 MPa. The supercritical state was maintained for 1 h, and the autoclave was decompressed and cooled to room temperature and atmospheric pressure.

2.2. Characterization

The morphology of the composite aerogel was characterized by using scanning electron microscopy (SEM: S-4800, Hitachi, Japan) and transmission electron microscope (TEM: JEM-1200EX, JEOL, Japan). The crystal phase was analyzed by powder X-ray diffraction (XRD: Empyrean 200895, PANalytical B.V., Holland) with the use of Cu Kα radiation (λ = 1.5418 Å) at 4°/min scanning speed in the 2θ range from 10° to 90°. The surface areas and pore structures were characterized by N_2 adsorption-desorption isotherms (OMNISORP100CX, Beckman Coulter, USA) and mercury injection capillary pressure method (AutoPore IV 9510), the detail data analysis was based on Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The average pore diameters and cumulative pore volumes were calculated using the desorption branch of the isotherm. The thermal conductivity of the sample was measured using the transient hot-wire technology (TC3000, XIATECH, China). The stress-strain curve and the elastic moduli of the samples were characterized by using electronic universal testing machine (AG-1, Shimadzu Corporation, Japan).

3. Results and discussion

To prepare monolithic composite aerogel, the wet gel was aged in TEOS according to previous literature [13–15]. It is found that crack-free aerogel monoliths can be obtained after supercritical drying the wet gel aged in TEOS, when the aerogel obtained from the wet gel without aging in TEOS showed obvious cracks (Fig. S1). EDX characterization shows that the silicon content in the crack-free aerogel is ~5.5% wt, which equals to ~11.8% wt of silica remains in the sample after soaking in TEOS. Fig. 1 is the snapshot of the as-prepared micro-nano YSZ-Al_2O_3 composite aerogels with various ZrO_2/Al_2O_3 molar ratios. Without adding YSZ aerogel, the aerogel-like alumina monolithic can be obtained, which coincides with that in literature [18]. When the molar ratios of ZrO_2:Al_2O_3 were 1:5 and 1:2.5, crack-free monolithic composite aerogel as large as 3.3 cm in diameter can also be formed, as shown in Fig. 1(a) and (b). The bulk densities of ZA-1 and ZA-2 are 0.141 g/cm^3 and 0.152 g/cm^3, which are slightly higher than that of ZA-0 (0.135 g/cm^3), but are still within the range of reported aerogel materials [19–21]. However, further increasing the ratio of ZrO_2 to ZrO_2:Al_2O_3 = 1:1.25 led to fragile monolith as shown in Fig. 1(c), which easily fractured during the supercritical drying process. Such observation implies that the filling of YSZ aerogel must have altered the microstructure of the original Al_2O_3 hollow microspheres.

Such speculation was confirmed by SEM characterization. The corresponding SEM images of micro-nano YSZ-Al_2O_3 composite aerogels with various molar ratios of ZrO_2:Al_2O_3 are shown in Fig. 2. Fig. 2(a) shows pristine aerogel-like alumina (ZA-0) with

Table 1
Starting compositions of samples (ZA-0, ZA-1, ZA-2, ZA-3).

	W_{PEO}(g)	$W_{AlCl3\cdot6H2O}$ (g)	$W_{ZrOCl2\cdot8H2O}$ (g)	$W_{Y(NO3)3\cdot6H2O}$ (g)	V_{EtOH} (ml)	V_{H2O} (ml)	V_{FA} (ml)	V_{PEG} (ml)	V_{PO} (ml)
ZA-0	0.549	19.5	0	0	24.5	19.5	0	0	33.0
ZA-1	0.549	19.5	2.6	0.68	46.5	25.0	0.16	0.86	38.5
ZA-2	0.549	19.5	5.2	1.36	67.5	30.0	0.32	1.72	44.0
ZA-3	0.549	19.5	7.8	2.04	89.5	36.0	0.48	2.58	49.5