Ceramics International xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Ceramics International

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

Novel self-reinforcing ZrO_2–SiO_2 aerogels with high mechanical strength and ultralow thermal conductivity

Xianbo Hou[a], Rubing Zhang[a,*], Baolin Wang[b]

[a] School of Civil Engineering, Beijing Jiaotong University, 100044, Beijing, China
[b] Graduate School at Shenzhen, Harbin Institute of Technology, Harbin 150001, China

ARTICLE INFO

Keywords:
ZrO_2–SiO_2 aerogels
Multiple impregnation
Mechanical property
Thermal property

ABSTRACT

Novel self-reinforcing ZrO_2–SiO_2 aerogels with high mechanical strength and ultralow thermal conductivity are fabricated by impregnating hydrolyzed ZrO_2–SiO_2 sol into wet gel matrix and drying. The ZrO_2–SiO_2 sol fills the macropores and defects of ZrO_2–SiO_2 aerogel matrix generating during the gelation process, which contributes to the improvement of the mechanical properties of the ZrO_2–SiO_2 aerogel matrix. The mechanical and thermal properties of the as-prepared ZrO_2–SiO_2 aerogel are investigated and discussed. The results show that the mechanical strength of the self-reinforcing aerogels obviously increases from 0.51 to 3.11 MPa with the increase of impregnation times, while the thermal conductivity of the aerogels slightly increases from 0.0235 to 0.0306 $W\,m^{-1}\,K^{-1}$. The novel self-reinforcing ZrO_2–SiO_2 aerogel could have interesting applications in aerospace and energy because of its outstanding mechanical and thermal properties.

1. Introduction

Recently, ZrO_2–SiO_2 aerogels have attracted great attention for thermal insulation in the fields of energy technology, aerospace, and construction etc., because of their outstanding properties such as superhigh porosity, low density, high specific surface area, and ultralow thermal conductivity [1–5]. ZrO_2–SiO_2 aerogels have complicated three-dimensional nanoporous structure, which results in its extremely low thermal conductivity [6–8]. Additionally, they exhibit better heat-insulation properties compared with other aerogels because zirconia has a higher temperature resistance and unformed silica effectively restricts the phase transition and crystal growth of zirconia [9,10]. Zu et al. [11] fabricated a thermally stable ZrO_2–SiO_2 aerogel and maintained a high specific area of 172 m^2/g and a large pore volume of 0.97 cm^3/g after heat treatment at 1000 °C. However, similar to silica aerogels [12] and Al_2O_3 aerogels [13], ZrO_2–SiO_2 aerogels are inherently fragile and break at a relatively low stress because of their weak nanoporous structure. This seriously restricts the widespread application of ZrO_2–SiO_2 aerogels as outstanding thermal insulation materials [14].

Many studies are underway to improve the mechanical properties of aerogel materials [15,16]. And different kinds of reinforcing phases such as whiskers [17], fibers [18], nanotubes [19], and particles [20], are added into the aerogel matrix to strengthen the pure aerogel. It can be noted that the mechanical properties of the aerogel are obviously improved. However, these reinforcing methods have some disadvantages. As the reinforcements are added into the aerogel matrix, the heat transfer paths are obviously increased, which has a negative influence on the thermal insulation properties of the aerogel matrix. Yuan et al. [21] fabricated silica aerogel/glass fiber composites by press forming of silica aerogel powders and dispersing glass fibers. The mechanical strength of the aerogel composites was improved at the cost of the obvious increase of thermal conductivity. Hou et al. [17] fabricated whisker-reinforced Al_2O_3–SiO_2 aerogel composites with a high compressive strength (0.26–1.40 MPa) and a relatively low thermal conductivity (0.027–0.049 $W\,m^{-1}\,K^{-1}$). Although the mechanical strength of these composites was improved, the thermal conductivity of the composites sharply deteriorates while the density increases. Furthermore, the reinforcements, such as short-cut fibers and whiskers, are dispersed by mechanical agitation, which are inhomogeneous in the gelation process. The addition of the reinforcements unavoidably destroys the continuous nanostructure of the aerogel matrix, which adversely effected the properties of aerogel matrix. More importantly, the reinforcement can hardly bond with the aerogel matrix because of the lacking compatibility between the two materials [22]. The differences in the shrinkage ratios between the reinforcements and the aerogel matrix could increase the cracks and defects, which is detrimental for the mechanical properties of the aerogel composites.

To the best of our knowledge, an aerogel matrix with high mechanical strength and outstanding heat-insulating property has not been

* Corresponding author.
E-mail address: zrb86411680@126.com (R. Zhang).

https://doi.org/10.1016/j.ceramint.2018.05.199
Received 8 April 2018; Received in revised form 15 May 2018; Accepted 23 May 2018

successfully fabricated. In this study, we report a novel route to strengthen ZrO_2–SiO_2 aerogel matrix by optimizing its microstructure. The novel self-reinforcing ZrO_2–SiO_2 aerogel is prepared by impregnating ZrO_2–SiO_2 sol into ZrO_2–SiO_2 wet gel to form composite ZrO_2–SiO_2 aerogel. The results indicate that the multiple impregnations could effectively eliminate the macropores and defects in the aerogel matrix and greatly improve the mechanical properties of ZrO_2–SiO_2 aerogels. The microstructure, mechanical properties, and heat transfer mechanism of the ZrO_2–SiO_2 aerogel are studied.

2. Experimental procedures

2.1. Raw materials

Tetraethoxysilane (TEOS), zirconyl chloride octahydrate ($ZrOCl_2{\cdot}8H_2O$), ethanol, acetic acid, polyethylene glycol 400 (PEG 400), formamide (FA), and 1,2-epoxyporopane (PO) were purchased from Sinopharm Chemical Reagent Co. Ltd., China. All chemical reagents used in this work are analytical reagent and all chemicals are used as the received without further purification.

2.2. Preparation of ZrO_2–SiO_2 aerogels

TEOS and $ZrOCl_2{\cdot}8H_2O$ were used as the silicon and zirconium precursors, respectively. ZrO_2–SiO_2 aerogels with ultralow thermal conductivity were prepared via a sol–gel method, followed by supercritical drying. First, the silica sol was prepared by hydrolyzing TEOS in an ethanol–aqueous solution. TEOS, H_2O, ethanol, acetic acid was directly mixed with a mole ratio of 1:5:10:2. Then, $ZrOCl_2{\cdot}8H_2O$ was dissolved into the ethanol–aqueous solution to prepare a zirconia sol, which was added to the silica sol to obtain the ZrO_2–SiO_2 sol. The mole ratio of ZrO_2 and SiO_2 is 1:1. FA and PEG 400 were orderly added to the ZrO_2–SiO_2 sol as dry control chemical agent and dispersant, respectively. After stirring, PO was added to the ZrO_2–SiO_2 sol as a gelation promoter. The sol was allowed to gel for several minutes. The obtained ZrO_2–SiO_2 wet gel was aged for several hours in molds. Then, the wet gels were replaced with ethanol for 3 days and subsequently modified with a TEOS/ethanol solution (1:1 by volume). Subsequently, the wet gels were exchanged with ethanol for 2 days. After aging, solution exchange and supercritical drying, the ZrO_2-SiO_2 aerogels are prepared.

2.3. Preparation of the self-reinforcing ZrO_2–SiO_2 aerogels

The wet gels obtained above were carefully moved to the ZrO_2–SiO_2 sol to avoid the destruction of wet gels. The ZrO_2–SiO_2 sol was synthesized with the same proportion as the wet gel. The hydrolyzed sol replaced ethanol in the wet gel several times, and the impregnation process was not complete until the wet gel was saturated with the ZrO_2–SiO_2 sol. When the ZrO_2–SiO_2 wet gel was immersed into the ZrO_2–SiO_2 sol, the sol replaced ethanol in the nanostructure of the wet gel. Subsequently, the wet gel—impregnated with the ZrO_2–SiO_2 sol—was moved into an oven at 60 °C. The sol immersed into the ZrO_2–SiO_2 wet gel could gel within 24 h. After gelation, the ZrO_2–SiO_2 sol, filled in the wet gel, bonded with the original wet gel, exhibiting an excellent compatibility because the ZrO_2–SiO_2 sol and ZrO_2–SiO_2 wet gel were prepared with the same proportion. The as-prepared wet gel was then modified for 2 days in a 1:1 TEOS/ethanol solution (by volume). And then, the as-prepared wet gel is exchanged by ethanol two times a day. Finally, aging, solution exchange, and supercritical fluid drying were applied to yield the composite ZrO_2-SiO_2 aerogel. The obtained aerogel composites are referred to as ZrO_2–SiO_2–X, where X stands for the number of times impregnation was performed, e.g., ZrO_2–SiO_2–0 is the initial aerogel, whereas ZrO_2–SiO_2–2 is an aerogel composite that was impregnated two times. Fig. 1 shows the preparation process of the self-reinforcing ZrO_2–SiO_2 aerogels that were fabricated via impregnation.

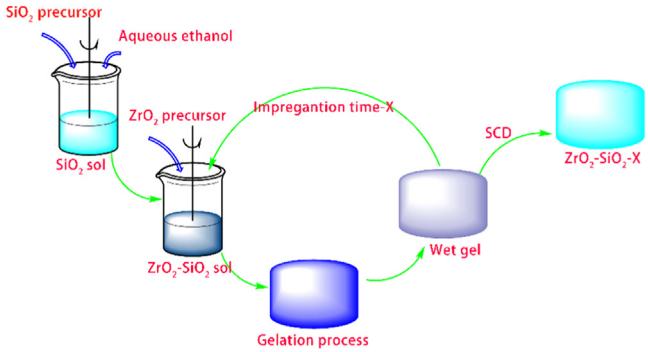

Fig. 1. Flow chart of the prepare processing for ZrO_2-SiO_2 aerogel fabricated by impregnation method.

2.4. Characterization

The obtained ZrO_2–SiO_2–X aerogels were observed via scanning electron microscopy (FEI Quanta 200; FEI Company, Hillsboro, USA) to analyze their microstructure. The density of the composite aerogel was determined on the basis of the weight and the corresponding volume of the samples. Room-temperature thermal conductivity tests were performed at 25 °C using a thermal conductivity instrument (DRE-III; Xiangtan Xiangyi Instrument Co., Ltd., Xiangtan, China). The compressive strength of the cubic samples (10mm × 10mm × 10mm) was measured using a testing machine (Zwick Z050; Zwick, Ulm, Germany) with a crosshead speed of 1.0 mm min^{-1}. In the experiments, more than six samples of each measurement were selected to obtain the average value.

3. Results and discussion

3.1. Properties of the self-reinforcing ZrO_2–SiO_2 aerogels

Fig. 2 shows the self-reinforcing ZrO_2–SiO_2 aerogels and the illustration of the impregnation process. As shown in Fig. 2(a–d), self-reinforcing ZrO_2–SiO_2 aerogels were successfully prepared via multiple impregnations and the ZrO_2–SiO_2–X composites were crack free and intact, which indicates that impregnation does not destroy the aerogels. As shown in Fig. 2(e–h), immersing the ZrO_2–SiO_2 sol into the wet gel gradually filled the pores and decreased the number of defects in the aerogels.

Table 1 summarizes the variations in linear shrinkages, porosities, and densities for ZrO_2–SiO_2 aerogels with different impregnation times. The density of the ZrO_2–SiO_2 aerogels sharply increased from 0.16 g/cm^3 of ZrO_2–SiO_2–0 to 0.46 g/cm^3 of ZrO_2–SiO_2–3, and the porosity of the ZrO_2–SiO_2 aerogels decreased from 96.4% to 89.6%. This can be attributed to an increase in the solid content of the aerogels after multiple impregnations. Furthermore, different from the traditional aerogels, the linear shrinkage of the as-prepared aerogels obviously decreased from 21.3% to 8.9% during the multiple impregnation process. Because the multiple impregnation process increases the density of the ZrO_2–SiO_2 aerogels and improves the strength of the nanostructure network, the backbone of the aerogel becomes stronger and is able to resist the capillary pressure in the nanopores. As a result, the linear shrinkage naturally decreases with increasing impregnation times. As summarized in Table 1, with the increase of impregnation times, the density of the as-prepared aerogels increased from 0.16 to 0.46 g/cm^3, the thermal conductivity of the ZrO_2–SiO_2 aerogels first decreased from 0.0235 to 0.0231 W m^{-1} K^{-1} and then increased to 0.0306 W m^{-1} K^{-1} and the compressive strength increased from 0.51 to 3.11 MPa.