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Porous silica ceramics with closed-cell structure prepared by inactive hollow spheres for heat insulation

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ABSTRACT

Highly porous silica ceramics (PSCs) with closed-cell structure are fabricated via sintering of randomly packed hollow SiO_2 spheres (HSSs), and the influences of sintering parameters, additives and physical features of HSSs on the structure and performance of prepared PSCs are discussed. The results show that the hollow structure of SiO_2 spheres is reserved during the sintering process due to its low-activated shells and the sintered necks are finely formed among the hollow spheres, which results in both high porosity and superior strength of final products and thus meets the needs of heat shielding materials. In addition, the optimized PSCs are synthesized with sintering temperature of 1200–1250 °C and additive of 4 wt.% H_3BO_3 combining 6 wt.% Al_2O_3, and the increase of closed porosity of PSCs brings in the enhanced thermal shielding effect while the strength degrades. Furthermore, the structure analysis reveals that decreased cristobalite phase in the PSCs reduces the glass viscosity and increases the packing density of HSSs, which also prefers to enhance the mechanical strength and thermal insulation. As a result, thermal conductivity of about 0.102–0.218 W/(m·k) and compressive strength of 3.2–14 MPa are obtained in our synthesized products.

1. Introduction

Porous silica ceramics are ideal candidate for thermal protection systems by virtue of low density, low thermal conductivity and excellent thermal-shock resistance [1–3], and widely applied in insulation for furnaces, fire protection and thermal-mechanical aerospace structures, etc. [4–6]. It is noted that porous ceramics can be classified as either open- or closed-cell based on their structural property. In contrast to open-cell structures, closed-cell structures have advantages in strength and heat insulation due to their load-bearing cell walls [7–9], and received considerable attentions in recent years. Generally, porous silica ceramics can be efficiently fabricated using hollow beads, in which hollow spheres are added as pore forming agents into ceramic matrix, and the closed pores are reserved after hollow spheres melt into matrix. The merit of this method is the purposeful control of pore size and content through adjusting size distribution and content of hollow spheres into matrix, thus the precise control of the hollow precursor is critical to the structure and properties of obtained porous ceramics [1].

Nowadays, the ceramic hollow spheres derive from a wealth of sources, including industrial waste from coal and large numbers of preparation technologies [10]. At present, fly ash cenospheres (20–300 μm) as industrial waste are extensively applied in the forming of closed pores. However, due to its low crush strength (10–35 MPa) [11] derived from the micropores on shells, the doping content of fly ash cenospheres is usually restricted for acceptable mechanical strength [1,12,13], and thus the porosity is dissatisfied to the insulation performance. Furthermore, the pores inside fly ash suffer shrinkage or are completely destroyed during heat treated process [14] owing to its porous and active shells. For example, Yang Yuan et al. [15] fabricated a kind of thermal insulation wall material with 65 wt.% fly ash added at 1050 °C, however its porosity decreased to about 40–50% and the thermal conductivity reached as high as 0.88 W/(m·K). Figen Balo et al. [16] manufactured one type of insulation material with 60 wt.% of fly ash cenospheres added, the compressive strength was in the range of 1.11–10.01 MPa while the corresponding thermal conductivity was all higher than 0.313 W/(m·K). The hollow ceramic sphere synthesized by usual preparation technologies just like chemical

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methods [17–20] and sacrificial core template [21–24], have similar problems that its porous shells and large surface area bring in insufficient strength and high sintering activity respectively. In addition, coarse hollow spheres with dense shell and larger diameter (1–10 mm) can be prepared by coaxial nozzle process [25], however these spheres also cannot get rid of large amount of matrix powders for lacking of sintered necks per unit volume. Hence, the hollow spheres with dense shell, lower activity and smaller size are important for the preparation of close-cell structured ceramics which have both sufficient strength and high porosity.

In our earlier work, hollow SiO_2 spheres (HSSs, 20–150 μm) with dense shell, high closed porosity, high strength and relatively lower activity were prepared by thermal plasma technology [26]. In this work, the synthesized HSSs were adopted as both matrix and pore forming agent for the preparation of porous silica ceramics (PSCs). The PSC is designed to be structured by sintered compact HSSs, which not only results in closed-cell structure to ensure mechanical strength, but also leads to relatively high porosity to guarantee heat insulating performance. However, the difficulty exists that the inactive shells are hard to be sintered forcefully before the crystallization temperature of cristobalite and thus the ceramic strength cannot be enhanced simply through increasing sintering temperature. Therefore, moderate additives are needed to promote the formation of necks and suppress the cristobalite. Finally, the designed PSCs were successfully synthesized and the structure of PSCs was revealed.

2. Experimental procedure

2.1. Materials

In this work, HSSs were prepared via a two-step method combining spray drying and DC thermal plasma sintering, and the process conditions were shown in our earlier publication [26]. H_3BO_3 (Beijing Chemical Works, China) was used as fusing agent to promote the formation of sintered necks. $Na_2SiO_3 \cdot 9H_2O$ (Beijing Chemical Works, China) and nano-Al_2O_3 (VK-L30, JingRui Co., Xuancheng, China) were attempt to inhibit cristobalite. In gelcasting process, acrylamide (AM, $C_2H_3CONH_2$) and N,N′-methylenebisacrylamide (MBAM, $(C_2H_3CONH)_2CH_2$) were employed as monomers in gel-casting. Ammonium persulfate (APS) and tetramethylethylenediamine (TEMED) were applied as initiator and catalyst, respectively. All chemicals used in this study were analytical (AR) grade.

2.2. Preparation of porous SiO_2 ceramics

The preparation procedure of PSCs is illustrated in Fig. 1. To begin of all, AM and MBAM (mass ratio 30:1) were dissolved in deionized water, and a 5 wt.% premix solution of AM was obtained. Secondly, the HSSs, fusing agent, inhibitor, moderate TEMED and ammonium persulfate were added into appropriate amount of premix solution successively and stirred sufficiently. The viscosity of slurry was about 350 mPa s which could keep HSSs stabilization before gelled. Thirdly, the slurry was kept at 60 °C for 30 min to polymerize to gelled body, and then the green body was produced after dried. Subsequently, the samples containing organic binder were heated at a heating rate of 2 °C/min from 20 to 550 °C under air atmosphere, and then the heating rate was accelerated to 8 °C/min from 550 to 1230 °C. Finally, PSCs were achieved after a dwell time of 2 h.

2.3. Characterization

Scanning electron microscopy (SEM, JEOL, JSM-6700F) was used to observe the morphology of HSSs and the fracture surfaces of PSCs, and their internal structures were observed by Backscatter electron (BSE) detectors under the background of epoxy resin. X-ray diffractometer (XRD, PANalytical, X′ Pert PRO MPD) was applied with a scanning speed of 8°/min to identify the phase composition of HSSs and phase development of silica ceramics during heat-treated process. Laser particle size analyzer (Beckman Coulter, LS 13 320) was used to determine the particle size distribution. The density of HSSs (ρ_{HSS}) was measured by a pycnometer (Micromeritics, AccuPyc 1340), and the density of solid material of HSSs ($\rho_{s\text{-}HSS}$) and synthesized PSCs ($\rho_{s\text{-}PSC}$) could also been measured after milled and sieved by 400 mesh sieve. The bulk density of PSCs (ρ_c) was calculated by weight and dimensional measurements, and the open porosity (ε_o) was measured using water displacement method. To reveal the formation process of necks, EDS (INCA Microanalysis Suite) was applied to analyze the element distribution.

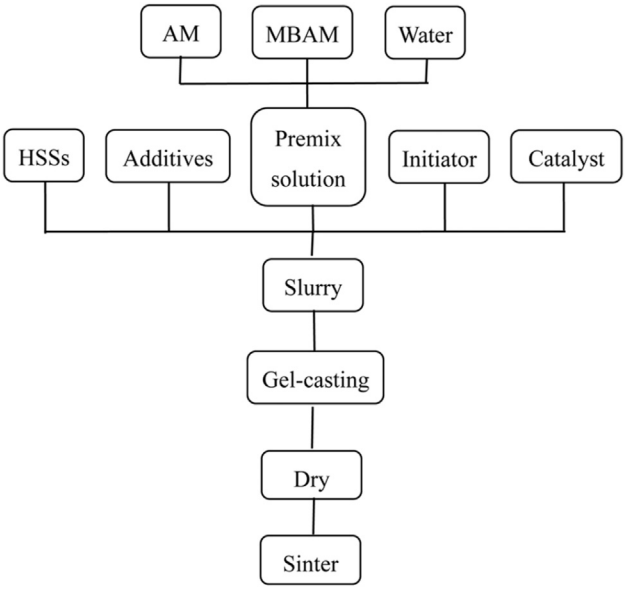

Fig. 1. The fabrication diagram of PSCs.

In order to investigate the change of sphere size after sintering, multi-step calculations were carried out. Firstly, the total porosity of PSCs (ε) was calculated according to equation (1) and the closed porosity of PSCs (ε_c) was ε-ε_o.

$$\varepsilon = 1 - \rho_c/\rho_{s-PSC} \quad (1)$$

Secondly, the average closed porosity of hollow spheres on PSC ($\varepsilon_{c\text{-}PSC}$) was calculated by:

$$\varepsilon_{c-PSC} = \varepsilon_c /(1-\varepsilon_o) \quad (2)$$

Meanwhile, the average inner diameter (D_1) and outer diameter (D_2) of HSS after sintering satisfy the relation (3) and (4), which is based on the definition of closed porosity and the relationship of mass conservation, respectively.

$$\left(\frac{D_1}{D_2}\right)^3 = \varepsilon c - PSC \quad (3)$$