Thermal stability of hollow YSZ microspheres and processing of their porous materials

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ABSTRACT

Hollow yttria-stabilized zirconia (YSZ) microspheres with a diameter of 1.2–5.1 μm and a wall thickness of about 125 nm were synthesized, and their thermal stability was revealed for a hold time of 1 h at temperatures of 800°C, 1000°C and 1200°C. The microspheres were then used as raw materials to prepare bulk porous ceramics by gelcasting processing. The effects of the solid loading contents and sintering temperatures of the hollow YSZ microspheres on the microstructures, porosity, compressive strength and room-temperature thermal conductivity of the porous ceramic materials were investigated. Increases in the solid contents and sintering temperatures were found to decrease the bulk porosity and number of larger pores. Porous materials made with hollow spherical powders exhibited porosities ranging from 61.50% to 90.17%, with a peak value of 90.17% obtained under a solid loading of 5 vol% at a sintering temperature of 1100°C. The experimental thermal conductivity as a function of porosity was within the ranges predicted by one form of the Maxwell-Eucken model (Maxwell-Eucken 1) and the effective medium theory (EMT), reaching the lowest value of 0.052 W/(m·K) at a porosity 90.17%.

1. Introduction

Porous zirconia materials exhibit excellent chemical stability, good corrosion resistance and low thermal conductivity with a slight dependence on temperature across a broad range [1]. They have been studied extensively for wide-ranging industrial and medical applications such as thermal barrier coatings [2], ceramic filters [3], catalyst supports and membranes for gas filtration [4], solid oxide fuel cells [5] and biological scaffolds [6]. Various processing techniques have been developed to fabricate porous zirconia ceramics, including the replication [7], gelcasting [8], freeze-casting [9,10], sacrificial natural or artificial pore-formation [11] and direct-foaming methods [12], as categorized in several reviews and monographs [13–15].

Pore volume fractions between 45% and 75% using nanometric-sized yttria-stabilized zirconia (YSZ) grains mixed with a commercial latex were achieved, and the materials showed a room-temperature thermal conductivity value approaching a lower limit of 0.1 W/(m·K) [16]. Organic additive burning during thermal treatment yielded pores that were mostly smaller than 1 μm in diameter [17]. Gel-casting of YSZ nanopowder and polymethylmethacrylate (PMMA) sacrificial templates as starting suspensions revealed homogeneous microstructures after drying, burn-out and sintering, characterized by grain sizes smaller than 200 nm with a macropore diameter of around 1 μm and closed porosity of between 10% and 20% [11]. Garrido et. al [17], used starch as a fugitive filler and binder in a direct-casting process to produce porous YSZ ceramics. The volume fraction of porosity in their sintered compacts was between 0.48 and 0.65, depending on the starch volume fraction in the green body as well as on the sintering temperature. Unlike such sacrificial template methods, water- [18] and tert-butyl alcohol (TBA)-based [19] gelcasting of porous YSZ ceramics, combined with monodisperse PMMA microspheres as both pore-forming and lubricating agents [20] were shown to be effective for fabricating low thermal conductivity ceramics. Thermal conductivity may range from 0.06 to 0.65 W/(m·K) [16,19,20] with adjustment of various processing conditions.

Since materials with a hollow structure exhibit such superior properties as even lower density, higher specific surface area and larger surface permeability compared to their conventional solid counterparts [21], hollow ZrO₂ microspheres of various diameters have been developed using both template [22–24] and template-free methods [25–27]. Li and Wang [28] have achieved ultralow thermal conductivity of 0.030 W/(m·K) at room temperature by molding and uniaxially cold-pressing hierarchically porous YSZ hollow spheres with outer diameters of several hundred nanometers to fabricate samples for thermal conductivity measurement. These sub-micrometer-sized
porous YSZ hollow spheres show limited thermal stability, however, as exemplified by rapid coarsening and growth of the spheres at around 600°C [22–24,28]. Since zirconia-based materials are of considerable interest in high-temperature applications, the thermal stability of hollow ZrO$_2$ microspheres at higher temperatures and of sintered bulk porous materials warrant further investigation. In the present work, hollow yttria-stabilized zirconia microspheres with micrometer-sized diameters were synthesized and their thermal stability was investigated. The microspheres were then used as starting materials to prepare porous ceramics by gelcasting processing. The effects of the solid loading contents and sintering temperatures on the microstructures, porosity, compressive strength and room-temperature thermal conductivity of the ceramic materials were studied.

2. Experimental procedures

2.1. Materials

Zirconium oxychloride (ZrOCl$_2$ · 8H$_2$O), yttrium nitrate hexahydrate (Y(NO$_3$)$_3$ · 6H$_2$O), absolute ethanol, hydrochloric acid and urea were used to synthesize hollow YSZ microspheres. For gelcasting of porous bulk YSZ materials, tertbutyl alcohol (TBA) was employed as a solvent and pore-forming agent, N,N,N′,N′-tetramethylethylenediamine (TEMED) as a gelation catalyst, N-methylol acrylamide (N-MAM) as a monomer, ammonium persulfate (APS) as a reaction initiator, and N,N,N′-methylenebisacrylamide (MBAM) as a crosslinker. All analytical grade chemicals were used as received without further purification. Industrial grade ZrO$_2$ fibers with diameters of were ground and sieved to produce final short-fiber reinforcement. MnO$_2$ powders were used as a sintering aid. The specifications and suppliers of the above materials and raw materials are shown in Table 1.

2.2. Materials preparation and characterization

2.2.1. Preparation of hollow microspheres

Synthesis of hollow microspheres was conducted based on the procedures in Ref [27], except for the addition of Y(NO$_3$)$_3$ · 6H$_2$O as a new reactant. In a typical synthesis, 2.0 g ZrOCl$_2$ · 8H$_2$O, 0.24 g Y(NO$_3$)$_3$ · 6H$_2$O and 0.6 g urea were dissolved in 40 ml absolute ethanol, and 10 ml 36.5% hydrochloric acid was then added to the solution under vigorous stirring. After stirring for 5 min at room temperature, the solution was transferred to a 100-ml Teflon-lined stainless-steel autoclave. The autoclave was then sealed and heated in an oven at 160°C for 12 h to enable hydrothermal synthesis. After cooling down naturally to room temperature, the production solution was moved to a glass beaker for drying in an oven at 60°C to recover white precipitates. The dried powders were then calcined in a muffle furnace for 1 h at 800°C, 1000°C and 1200°C, respectively, for a thermal stability study.

In fabricating large quantities of powders to process bulk porous specimens for mechanical testing and thermal conductivity measurement, the above method was scaled up. A 300-ml Teflon-lined stainless-steel autoclave was used to handle hydrothermal reactants of 10.0 g ZrOCl$_2$ · 8H$_2$O, 1.2 g Y(NO$_3$)$_3$ · H$_2$O and 3.0 g urea in 200 ml absolute ethanol and 50 ml hydrochloric acid, with other procedures remaining the same as in the above small-lot production. The powders were heat-treated in a muffle furnace for 1 h at 1000°C to prepare porous bulk materials.

2.2.2. Preparation of porous bulk materials

A TBA-based solution was prepared by adding 14.5 wt % N-MAM and 0.5 wt% MBAM to TBA. Solid loadings consisting of 87 wt% ZrO$_2$ microspheres, 10 wt% ZrO$_2$ short fibers and a sintering aid of 3 wt% MnO$_2$, unless specified otherwise, were mixed and added to the premixed solution to produce suspensions with solid

### Table 1. List of materials, their specifications and suppliers.

| Name                  | Specification | Suppliers                                      |
|-----------------------|---------------|------------------------------------------------|
| ZrOCl$_2$ · 8H$_2$O   | 98.0%         | Aladdin Reagent Co., Ltd (Shanghai, China)     |
| Y(NO$_3$)$_3$ · 6H$_2$O| 99.9%         | Chengdu Chron Chemicals Co., Ltd (Sichuan, China) |
| N,N,N′,N′-tetramethylethylenediamine | 97.0% | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
| Absolute ethanol hydrochloric acid | ≥99.0% | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
| Tertbutyl alcohol N,N,N′,N′-tetramethylethylenediamine | ≥99.7% | Sinopharm Chemical Reagent Co., Ltd (Shanghai, China) |
| ≥99.0% | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
| ≥98.5% | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
| N-methyl acrylamide | ≥99.0% | Nanjing Yulong New Materials Co., Ltd (Jiangsu, China) |
| Ammonium persulfate  | ≥98.0%        | Qinghe Andi Metals Co., Ltd (Hebei, China)     |
| ZrO$_2$ fiber         | Diameter 11-17 µm | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
|                       | Average length 460 µm | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
|                       | Average particle size 50nm | Shanghai Zhanyun Chemical Co., Ltd. (Shanghai, China) |
loadings of 5, 10 and 15 vol%. Vigorous stirring was conducted throughout the process.

In the gelcasting process, small amounts of the TEMED gelling catalyst and APS reaction initiator were added to the suspensions while stirring to promote monomer polymerization in molds at room temperature. The gelled green bodies were demolded and dried at 40°C in an oven until complete TBA volatilization. The dried samples were fired at 600°C for binder removal before final sintering at 1100°C, 1150°C, 1200°C, 1250°C and 1300°C for 2 h in a furnace. Porous bulk specimens were machined and finished to disks measuring 10 mm×10 mm×10 mm and 10 mm×10 mm×1 mm for strength and thermal conductivity measurements, respectively.

2.3. Characterization

The phases were analyzed using a BRUKER D8 Discover Advance X-Ray diffractometer (XRD) system (Germany), operated with Cu Kα (λ = 0.1541 nm) incident radiation at 30 mA and 40 kV. XRD data were acquired in the continuous scanning mode over the range of 20 to 90° (2θ) with a step width of 0.02° and a scan speed of 0.1°/s. Scanning electron microscopy (SEM, Sirion and FEI3D, FEI, Holland) was employed to observe the morphologies of the hollow zirconia microspheres and porous ceramics.

The porosity and density were calculated using the Archimedes method to determine the density of the porous samples, which was then compared to the density of the fully dense ceramic [29] taken as 6.0 g/cm³ [28] for this YSZ material. Compressive strength measurements were conducted with a universal testing machine (CMT4503, Sansi, China) with a crosshead loading speed of 0.5 mm/min.

The laser flash method was used to determine the effective thermal conductivity of the samples with the thermal diffusivity and specific heat measured at constant pressure with a Netzsch LFA 467 (Germany). A thin graphite coating layer was applied to the front and back surfaces of the sample to avoid laser radiation propagation through the thickness of the material and to improve the laser beam absorption. Cowan’s model [30] was used to calculate the thermal diffusivity from an analysis of the back surface temperature-time data. The thermal conductivity λ was then computed as follows:

\[ \lambda = \alpha \times \rho \times C_p, \]

where \( \alpha \) is the thermal diffusivity, \( \rho \) the density and \( C_p \) the specific heat of the material.

3. Results and discussion

3.1. YSZ microspheres

Figure 1 shows a typical XRD result for YSZ microspheres calcined at 1000°C for 1 h. Both the high-temperature tetragonal zirconia phase (JCPDS 48–0224) and low-temperature monoclinic phase (JCPDS 37–1484) were detected, a result in full agreement with those for recent metastable zirconia-yttria systems [31] for typically 5 mol% \( \text{Y}_2\text{O}_3 \), owing to the diffusionless mechanism.

Figure 2(a,b) reveal the morphologies of the YSZ microsphere product calcined at 800°C for 1 h. The microspheres display relatively smooth surfaces and diameters between 1.2 and 5.1 μm. They are aggregated to certain degrees, some of which obviously nucleate and develop concurrently during the hydrothermal processing prior to calcination. Their hollow structure is revealed by partial growth of some...
microsphere walls with open core-shell morphologies, as indicated by the arrows in Figure 2(a). Based on the magnified images in Figure 2(b), the microsphere wall is roughly 125 nm thick and apparently uniform and porous. Subsequent exposure to 1000°C for 1 h caused slight roughening of the microspheres’ outer surfaces (Figure 3) in comparison to those of the same magnification shown in Figure 2(b). This is believed to be due to the growth of individual grains making up the microsphere walls. Tiny holes also appeared in the smaller particles indicated by arrowheads. Heating at 1200°C for 1 h generated further grain growth, as is more clearly observed in Figure 4. The grain size measured for several individual grains in Figure 4 was 278 nm on average. This growth gave rise to a narrowing of the inner open space inside the hollow microspheres (insert in Figure 2(b)) and to microsphere particle disintegration due to diffusion depletion, as evidenced by the tiny holes in Figure 3. The formation mechanism for hollow structures is believed to be the same as that proposed in Ref [27].

3.2. Porous YSZ ceramics

3.2.1. Microstructure

Digital macroscopic images of porous YSZ ceramic samples with solid loadings of 0, 5 and 10 wt% ZrO₂ short fiber additions containing a sintering aid of 3 wt% MnO₂ and balance ZrO₂ microspheres, sintered at a temperature of 1200°C, are presented in Figure 5(a–c), respectively. It is clear that 10 wt% addition of ZrO₂ fiber contributes to the structural integrity of the sintered specimens (Figure 5(c)), in sharp contrast to the fragmented (Figure 5(a)) and cracked (Figure 5(b)) samples, because the ZrO₂ fiber helps to reduce sample contraction and cracking during the sintering process. Figure 5 also demonstrates a change in the color appearance of the bulk sample from pure white, like that seen in common ZrO₂ ceramic materials without MnO₂ addition, to a slightly yellow soil color in the presence of the MnO₂ sintering aid. Although not shown here, EDX composition analysis showed a uniform homogeneous distribution of elemental Mn in the range of 0.80–1.16 atomic weight percentage. The uniform yellow soil color in Figure 5 is believed to be related to uniform manganese distribution, the thermal decomposition of MnO₂ [32] and the Mn-doped ZrO₂ structure [33].

Typical microstructures of the bulk porous samples sintered at temperatures of 1100°C, 1200°C and 1300°C for a 10% solid loading are shown in Figures 6, 7 and 8, respectively. In Figure 6, the majority of hollow microspheres have kept their original shape and remained intact, with some particles broken and some pores formed in the shell walls due to YSZ grain growth and coarsening of the outer and inner hollow microsphere surfaces, as discussed in the preceding section. The left lower corner contains short fiber as reinforcement. By contrast, Figure 8(a,b) demonstrate much more critical grain growth and coarsening brought about by the 1300°C sintering
temperature, at which the hollow microspheres as a whole grew larger in diameter and the microsphere walls became thicker and partially broken. In the case of Figure 7, which shows microspheres sintered at 1200°C, grain growth and coarsening developed between the stages shown in Figures 6 and 8. The porosity in Figures 6, 7 and 8(a) can be categorized into two types, namely, a porosity originating between particles or particle aggregates similar to solid microspheres (indicated as “A”), and the other originating from hollow microspheres (indicated as “B”) due to hollow space inside the microspheres and pores formed in the hollow microsphere walls. Higher sintering temperatures cause A-type porosity to evolve in the form of typical sintering shrinkage and a decreased overall pore volume, because particle sintering leads to strengthening, densification and microstructure coarsening (Figures 6–8). B-type porosity is also expected to decrease at higher temperatures as grain coarsening in the wall reduces the volume of hollow space inside the microspheres and threatens to destroy the hollow structure, although the microsphere walls may develop a limited number of small pores.

To facilitate estimation of the pore and cavity sizes and distribution, the grey scales of Figures 6, 7 and 8(a) were adjusted to highlight pores and cavities by use of Adobe Photoshop imaging and graphic design software [34]. The reconstructed images shown in Figure 9(a–c) correspond to the original SEM results in Figures 6, 7 and 8(a), respectively, and reveal pores as dark regions. Both the volume and size of the pores decreased with increases in the sintering temperature. Most pore sizes in samples sintered at 1100°C are within the range of 2.0–10.0 μm (Figure 9(a)), which compares to the ranges of 2.5–5.0 μm (Figure 9(b)) for materials processed at 1200°C and of 1.5–2.5 μm (Figure 9(c)) for those sintered at 1300°C. Figure 10(a,b) represents a typical SEM micrograph and a reconstructed image of a 15% solid loading sample sintered at 1200°C. The grain growth and coarsening behavior of the hollow microspheres are similar to that of the 10% sample (Figure 7), but higher solid loading obviously leads to lower porosity due to further pore reduction and smaller pore sizes. The relationship between the bulk density and sintering temperature with changes in the solid loading volume of the hollow microsphere slurry is shown in Figure 11. The bulk density increases almost linearly with increases in the sintering temperature.
temperature up to 1200°C but varies more sharply at above this temperature. The porosity is reduced from 90.17% to 78.50%, and the bulk density is increased from 0.59 to 1.29 g·cm$^{-3}$ with increases in the solid loading volume from 5% to 15% at a sintering temperature of 1100°C. These trends can be clearly explained by the microstructural changes seen in Figure 6, 7, 8(a) and 10(a).

### 3.2.2. Compressive strength

Figure 12 shows the relationship between the compressive strength of bulk porous ceramics and the sintering temperature. With increases in the sintering temperature, the compressive strength increases from 0.55 MPa to 9.21 MPa for samples fabricated from a slurry loading of 5%, and the maximum strength of 39.32 MPa is obtained for materials calcined at 1300°C when the slurry loading is 15%. The enhancement of compressive strength in the case of higher sintering temperatures and slurry loadings is attributed to particle coalescence, reduction in pore sizes and densification of the pore walls, as evidenced in Figure 6, 7, 8 and 10(a). Also of note, the compressive strength increases nonlinearly, which corresponds to the change in behavior of the bulk density at 1200°C (Figure 11). The MnO$_2$ sintering aid was found to increase the strength by nearly 20% for a slurry loading of 10% and a calcination temperature of 1200°C, as compared to a sample without MnO$_2$ addition.

A model for the compressive mechanical strength of the ceramic foam can be expressed as a function of the relative density, as follows [35–38]:

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**Figure 9.** Reconstructed images produced by grey-scale adjustment to highlight pores and cavities. (a), (b) and (c) correspond to the original SEM images shown in Figures 5, 6 and 7, respectively.

**Figure 10.** Microstructure of a bulk porous sample sintered at 1200°C for 15% solid loading: (a) original SEM image and (b) its reconstructed image.

**Figure 11.** Effect of sintering temperature on bulk material density and porosity with varied solid loadings.

**Figure 12.** Relationship between compressive strength and sintering temperatures with varied solid loadings. Each strength datapoint was measured using a single sample.
where $\sigma$ and $\rho$ are the compressive strength and apparent density of the bulk porous material, respectively; the subscript "s" represents of the cell strut taken to be solid YSZ, and C is a dimensionless constant. $\sigma$ with respect to the normalized relative density $\rho/\rho_s$ is plotted on a logarithmical scale and shown in Figure 13. It can be fitted to a linear relationship with the exponent $n$ equal to 3.2, which is in a range similar to that of 1.90–3.18 [36–38] for porous materials manufactured from solid particles.

### 3.2.3. Thermal conductivity

Figure 14 displays the relationship between the porosity and thermal conductivity of porous YSZ ceramics, along with the values predicted from one form of the Maxwell-Eucken model (Maxwell-Eucken 1) [39] and the effective medium theory (EMT) equation [40]. While the EMT model is based on the assumption that neither of the two components in a heterogeneous system is necessarily continuous or dispersed, the Maxwell-Eucken 1 model represents a system in which the pores and ceramic particles are distributed uniformly, with continuous hollow YSZ microspheres and with air-trapping pores as the dispersed phase. The thermal conductivity of air and dense YSZ ceramics were taken to be 0.026 [41] and 2.2 W/(m·K) [42], respectively, in computing the results for the two theoretical models. The experimental thermal conductivities of the porous ceramics decrease with increases in the porosity and fall well within the ranges computed from the EMT equation and the Maxwell-Eucken 1 model. The lowest measured value is 0.052 W/(m·K) and the porosity is close to the EMT prediction at 90.17%, while all other experimental values deviate clearly from both the Maxwell-Eucken 1 and EMT models. The lower thermal conductivities at higher porosity can be explained by the microstructures developed within the porous YSZ ceramics displayed in Figure 6, 7, 8 and 10(a). Air-filled pores blocked heat transfer, and a large number of intergranular pores and hollow microsphere interfaces provided significant phonon and photon scattering [28], leading to better thermal insulation. Carson et. al [43] analyzed the effective conductivities of various internal porosity materials in which the condensed phase forms continuous conduction pathways, and found them to be bounded above the Maxwell-Eucken model 1 prediction and below the EMT model results. The experimented data obtained in the present study follow a similar pattern.

Since hollow microspheres have diameters ranging from 1.2 to 5.1 μm, the average diameter is taken to be 3.15 μm. The wall thickness of about 125 nm and slurry loadings of 5, 10 and 15 vol% should induce, in theory, additional closed porosity of 3.89, 7.78 and 11.68 vol%, respectively, in the bulk porous materials. Since a significant proportion of the hollow microspheres were broken in the processing, however, the actual closed porosity of the hollow microspheres must be reduced. More detailed modeling investigations taking into account the porosity due to the hollow microspheres will be necessary to quantitative comparisons with the thermal conductivity measurements.

The ultra-low thermal conductivity of 0.030 W/(m·K) obtained at room temperature for bulk samples of cold-pressed YSZ hollow spheres measuring several hundred nanometers in outer diameter [28] was due to the hierarchical meso- and nano-scale microstructures of the shells, since the YSZ hollow spheres were treated at only 500°C for 30 min. Ultra-low thermal conductivity is limited to the application at much lower temperatures than the materials studied here because the ZrO$_2$-related hollow microspheres in Ref. [28] show rapid coarsening and growth of the spheres at around 600°C for less than 2 h before the final
collapse of the hollow structure [22–24,28]. By comparison, most of the micrometer-sized porous YSZ hollow spheres in the present study survived thermal exposure from 800°C to 1200°C for 1 h. Our sintered high-strength bulk YSZ ceramics are suitable for application environments under mechanical loading and thermal stresses, moreover, which is a significant advantage over cold-pressed bulk samples with minimal mechanical strength.

4. Conclusions

(1) YSZ hollow microspheres calcined at 800°C for 1 h display smooth surfaces with diameters from 1.2 to 5.1 μm. While they largely maintain their hollow structure, exposure to higher temperatures of 1000°C and 1200°C, respectively, for 1 h leads to further grain growth and roughening of the microsphere wall.

(2) Hollow microspheres have been successfully employed to fabricate porous bulk YSZ ceramics through gelcasting processing. Solid loading contents and sintering temperatures play important roles in determining the bulk ceramic microstructure.

(3) Compressive strength ranges from 0.55 MPa to 39.32 MPa for bulk ceramics processed with the use of slurry loadings of 5%, 10% and 15% at calcination temperatures ranging from 1100°C to 1300°C. Strength as a function of relative density follows a power-law with an exponent of 3.2.

(4) The room-temperature thermal conductivity of the bulk porous materials as a function of porosity falls within the ranges predicted by one form of the Maxwell-Eucken model and the effective medium theory, and reaches its lowest value of 0.052 W/(m·K) at a porosity of 90.17%.

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