A novel highly porous ceramic foam with efficient thermal insulation and high temperature resistance properties fabricated by gel-casting process

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Abstract. The design of super thermal insulation and high-temperature resistant materials for high temperature furnaces is crucial due to the energy crisis and the huge wasting. Although it is told that numerous studies have been reported about various of thermal insulation materials prepared by different methods, the applications of yttria-stabilized zirconia (YSZ) ceramic foams fabricated through tert-butyl alcohol (TBA)-based gel-casting process in bulk thermal isolators were barely to seen. In this paper, highly porous yttria-stabilized zirconia (YSZ) ceramic foams were fabricated by a novel gel-casting method using tert-butyl alcohol (TBA) as solvent and pore-forming agent. Different raw material ratio, sintering temperature and soaking time were all investigated to achieve optimal thermal insulation and mechanical properties. We can conclude that porosity drops gradually while compressive strength increases significantly with the rising temperature from 1000-1500 °C. With prolonged soaking time, there is no obvious change in porosity but compressive strength increases gradually. All specimens have uniformly distributed pores with average size of 0.5-2μm and show good structural stability at high temperature. The final obtained ceramic foams displayed an outstanding ultra-low thermal conductivity property with only 200.6 °C in cold surface while the hot side was 1000 °C (hold 60 min to keep thermal balance before testing) at the thickness of 10 mm.

1. Introduction

For the past few years, high temperature heat insulation materials were widely used in many industrial fields, such as high-temperature kiln, metallurgy, aerospace, petrochemical and energy fields. The research and development of a super-low thermal conductivity and high-temperature resistant materials with a relatively high strength simultaneously is the top priority. Porous ceramics, known as a novel class of heat insulation materials, have attracted considerable attention because of its superior mechanical and thermal properties. Among them, yttria-stabilized zirconia (YSZ) ceramic foams, which have good chemical stability, light weight, good heat resistance, specific surface area, and good thermal shock properties, has been attracted much attention. However, the preparation of yttria-stabilized zirconia ceramic foams using traditional technology exists some shortcomings, like
stomatal distribution uniformity, low porosity, and so on. With tert-butyl alcohol (TBA, as solvent)-based gel-casting process is put forward in recent years as a new method for the preparation of porous ceramics\(^1\), we have noticed that the equipment of this molding process is simple and low-cost, and also the as-prepared products have high strength, uniform pore size distribution, high porosity, and slight pores.

At the same time, in consideration of induced neurotoxicity and environmental risks in the acrylamide system which is widely used as monomers in the traditional process, it is necessary to seek a new monomer to reduce/eliminate this hazard. The new monomer that can replace acrylamide must be soluble, and is able to form gel in solution. In view of the foregoing, we here choose low-cost N-hydroxymethyl acrylamide as monomer to replace acrylamide (AM), the experiments show that its toxicity is far lower than that of acrylamide (AM).

Herein, in this paper we use yttria-stabilized zirconia powder as raw materials, tert-butyl alcohol (TBA) as solvent and pore-forming agent to facile fabrication of ceramic foams with high porosity and slight pores. This novel method highlights in using low surface tension TBA solution as pore-maker without additional pore forming substance or solid pore former, which just need an ordinary drying process to achieve in-situ curing and the controllable of pore structure and uniform in the as-prepared green ceramic bodies. Series of characteristic experiments were proceeded (such as SEM, XRD, thermal conductivity, bulk density, porosity ) to analyze the morphology, physical and thermal properties, and the results showed the as-prepared YSZ ceramic foams are excellent both in thermal insulation and high-temperature resistance.

2. Experiment procedure

2.1. Materials
In our experiments, yttria-stabilized zirconia spherical powder with average diameter of ca.500-2000 nm was used as raw materials, while tert-butyl alcohol (TBA) as solvent and pore-forming agent, N-hydroxymethyl acrylamide as monomer, N, N'-methylenebisacrylamide (MBAM, \((\text{C}_2\text{H}_2\text{CONH})_2\text{CH}_2\)) as a crosslinker, initiator and catalyst for gelation reaction were ammonium persulfate (APS) and N, N, N', N'-tetraacetylethylenediamine (TEMED), respectively. All chemicals used in this study are AR grade. Briefly, through a simple gel-casting progress, we got yttria-stabilized zirconia (YSZ) ceramic foams, and then they were mold stripping drying, calcined at suitable temperature.

2.2. Fabrication
The detailed steps of gel-casting include preparation of premix, injection molding, drying and sintering. YSZ powder (solid content 32.5%, which is the optimal ratio in our study, the mass fraction, the same below) and premixed liquid (monomer, crosslinking agent and solvent mixture) were well-mixed through ball milling 2h, thus forming the solid content of 32.5% mass fraction slurry. Subsequently, the catalyst and initiator were added to the slurry while keep stirring evenly, and then pour it into the mold for curing 1 h, drying 12 h at an appropriate temperature before knockout. In the course of curing and drying, the monomer was polymerized, and in the meantime, the tertbutyl alcohol was volatile, and finally the ceramic green body with certain strength was formed. Finally, the fully dried green body was placed in a sintering furnace for sintering at 700 °C to preservation of 2 h, in order to make the polymer fully decomposed. Then slowly warming up to a predetermined temperature of 1200 °C for 2 h. Ultimately, samples were removed from the furnace to room temperature.

3. Results and discussion
The scanning electron microscopy (SEM) images of the obtained YSZ hollow spheres ceramic foam samples are shown in Fig.1a and Fig.1b. Fig.1a and b reveals the details of pore morphology and interconnection of grains in the ceramics. The spherical particles are mainly uniform, monodisperse and about 500–2000 nm in size. Also we can see from Fig.1b that adjacent particles in the surface
contact with each other to form a fused neck structure. The pores are connected with each other to form a stable three-dimensional network structure. This structure is formed due to the volatilization of TBA in the drying process, leaving irregular shape and interconnected pores, but the green body still has high strength owning to the winding of long chain structures in N-hydroxymethyl acrylamide between particles. In the process of degreasing, N-hydroxymethyl acrylamide decompose and further form interconnected pores, particles are overlapped to form loose three-dimensional network structure; In the following sintering process, the sintering neck structure is formed because of the interaction between particles, resulting in the original loose structure densification, and the strength enhanced. To further confirm the formation of yttria-stabilized zirconia (YSZ) hollow spheres, the cross-section in insert Fig. 1a can obviously reveal that, and also show that the thickness of hollow spheres is about 200-300 nm.

![Figure 1](image)

**Figure 1** (a) SEM and (b) the typical interconnection of grains images of yttria-stabilized zirconia (YSZ) hollow spheres ceramic foams. Inserts in (a) is the cross-section of typical single hollow sphere.

Fig. 2 shows X-ray diffraction (XRD) patterns of as-prepared YSZ hollow spheres ceramic foam samples before and after calcined at 1200°C for 2h, which is in good agreement with the standard data of tetragonal ZrO$_2$ (JCPDS No. 89-6976). The peaks of XRD patterns are very sharp, which indicates good crystallinity. As shown in Fig. 2, only t-ZrO$_2$ was detected in the sintered specimen. No extra characteristic peaks is detected from the patterns, indicating that there are no impurities in the products. There is no diffraction peak of yttrium oxide in Fig. 2, which shows that yttrium enters into the lattice of zirconia oxide. In addition, the XRD spectra of the zirconia oxide with no addition of yttrium oxide have both tetragonal and monoclinic phase diffraction peaks, which indicate that yttrium oxide plays a decisive role in stabilizing the crystal structure of zirconia oxide. These XRD findings are well matched to the reported results.
The porosity of as-prepared YSZ hollow spheres ceramic foams were calculated using mass and volume measurements to determine the relative density of the porous samples and then comparing those to the density of the original fully dense ceramic, which was taken as 6.0 g/cm³ for this YSZ material. According to this calculation method as shown in Table.1, the apparent densities of YSZ hollow spheres ceramic foams prepared by using TBA as solvent and pore-forming agent were range from 0.60-0.73 g/cm³. And the corresponding porosity varies from 87.8-90.0 %.

Different raw material ratio, sintering temperature and soaking time were all investigated to achieve optimal thermal insulation and mechanical properties. From our study, we can conclude that porosity drops gradually while compressive strength increases significantly when the sintering temperature raise from 1000-1500 °C. With prolonged soaking time from 2 h to 20 h as shown in Table. 1, there is no obvious change in porosity, which proves the good stability of structure and properties at a relative high temperature. In conclusion, we finally choose the sintering temperature of 1200 °C and holding 2 h as the optimal sintering condition. All specimens have uniformly distributed pores with average size of 0.5-2μm and show good structural stability at high temperature. Super-low thermal conductivity is obtained and high-temperature resistance with high strength makes it more applicable in high-temperature thermal insulating applications 6-8.

Table 1. Properties of fibrous YSZ hollow spheres foams with different sintering temperature and soaking time.

| Sintering temperature (°C) | Soaking time (h) | Apparent density (g/cm³) | Porosity (%) | Thermal conductivity (W/m·k) |
|----------------------------|-----------------|--------------------------|--------------|-----------------------------|
| 1000                       | 2               | 0.60                     | 90.0         | 0.040                       |
| 1200                       | 2               | 0.64                     | 89.3         | 0.038                       |
| 1200                       | 6               | 0.65                     | 89.1         | 0.041                       |
| 1200                       | 10              | 0.65                     | 89.1         | 0.042                       |
| 1200                       | 20              | 0.64                     | 89.3         | 0.042                       |
| 1500                       | 2               | 0.72                     | 88.0         | 0.045                       |
| 1500                       | 6               | 0.73                     | 87.8         | 0.046                       |

Thermal conductivity at room temperature was measured on the 6×6×3 mm surface grinding samples by using transient hot-wire method on TC3000E, and the samples must be dried fully at
150 °C for at least 8 h to make sure the water in the sample is volatilized due to the higher thermal conductivity of water. Through the multiple tests, the best sample we got was 0.038 W/m·k, which is much close to the thermal conductivity of air (0.026 W/m·k). And our samples are able to stay in high temperature (even to 1500°C) for a long time without any deformation and cracking. This is due to the high porosity and uniformly distributed small pores. In addition, compared with other reported ceramics foams, the structure of TBA-YSZ hollow spheres ceramics foams has longer heat transfer path and larger thermal resistance, which may enhance the photon scatting of the lattice.

Anyway, all these factors contribute to the low thermal conductivity of our products. There is an apocalypse that the thermal conductivity of our TBA-YSZ hollow spheres ceramics foams is comparable to the silica aerogel, and they also have many other advantages, like excellent thermostable performance and good infrared shading effect. Meaning while, TBA-YSZ hollow spheres ceramics foams could serve as the framework of silica aerogel to improve its mechanical properties, while not to reduce its super-low thermal conductivity.

To further evaluate the heat-shielding performance of the as-prepared YSZ hollow spheres ceramic foams, the back temperature difference of as-prepared test samples are measured by SMD thermocouple (accurate to 0.1°C). First, the samples must be prepared according to the size of 100×100×10mm, in order to match the door brick, we designed before. High temperature furnace is used as heat source. And the samples are placed in the middle-hole of the door brick, when the furnace is up to 1000°C, then we open the fire door to hold 60 min before test. This is because thermal equilibrium stability is necessary if you want to get an accurate test temperature. In addition, the right judgement of the figure is whether the number remain unchanged in at least 30 seconds. At last, the measured figure is the cold surface temperature of our ceramic foams. In this experiment, our as-prepared test samples have only 200.6 °C in cold surface while the hot side was 1000 °C (hold 60 min to keep thermal balance before testing) at the thickness of 10 mm, and the specimens keep a good surface condition and strength under the high temperature for a long time, suggesting that this kind of YSZ hollow spheres ceramic foams may exhibit a superior thermal insulation and high-temperature resistance performance for high temperature furnaces than any of other so-called high performance insulation materials.

4. Conclusion
In summary, highly porous yttria-stabilized zirconia (YSZ) hollow spheres ceramic foams were fabricated by a novel gel-casting method using tert-butyl alcohol (TBA) as solvent and pore-forming agent in this paper. Different raw material ratio, sintering temperature and soaking time were all investigated to achieve optimal thermal insulation and mechanical properties. We finally can conclude that porosity drops gradually while compressive strength increases significantly with the rising temperature from 1000-1500°C. With prolonged soaking time, there is no obvious change in porosity, but compressive strength increases gradually. All specimens have uniformly distributed pores with average size of 0.5-2μm and show good structural stability at high temperature. The final obtained ceramic foams displayed an outstanding ultra-low thermal conductivity property with only 200.6 °C in cold surface while the hot side was 1000 °C (hold 60 min to keep thermal balance before testing) at the thickness of 10 mm. Our present work indicated that yttria-stabilized zirconia (YSZ) hollow spheres ceramic foams were fabricated by a novel gel-casting method using tert-butyl alcohol (TBA) indeed have an positive effects on the high-temperature resistance abilities with a relative high strength, which may open up some new thoughts on the design of high-temperature resistance materials towards new energy-saving, high-temperature kiln, and green chemistry.

Acknowledgments
This work was financially supported by the Anhui Province Science and Technology Department, National Natural Science Foundation of China (NSFC).
References

[1] Y. Dong, C-A. Wang, J. Zhou and Z. Hong, A novel way to fabricate highly porous fibrous YSZ ceramics with improved thermal and mechanical properties, J. Eur. Ceram. Soc., 32 (2012), 2213–2218.

[2] Z. Sun, C. Lu, J. Fan, F. Yuan, Porous silica ceramics with closed-cell structure prepared by inactive hollow spheres for heat insulation, J. Alloy. Compd., 662 (2016), 157–164.

[3] L. Han, F. Li, X. Deng, J. Wang, H. Zhang, S. Zhang, Foam-gel casting preparation, microstructure and thermal insulation performance of porous diatomite ceramics with hierarchical pore structures, J. Eur. Ceram. Soc., 37 (2017), 2717–2725.

[4] W-L. Huo, X-Y. Zhang, Y-G. Chen, Y-J. Lu, W-T. Liu, X-Q. Xi, Y-L. Wang, J. Xu and J-L. Yang, Highly Porous Zirconia Ceramic Foams with Low Thermal Conductivity from Particle - Stabilized Foams, J. Am. Ceram. Soc., 99 (2016), 3512–3515.

[5] X. Du, L. Zhao, X. He, X. Wang, W. Qu, H. Chen, H. Chen, J. Wang, Z. Lei, A novel method based on ultrastable foam and improved gelcasting for fabricating porous mullite ceramics with thermal insulation–mechanical property trade-off, J. Porous. Mater., 23 (2016), 381–388.

[6] S. Liu, J. Liu, F. Hou and H. Du, Microstructure and properties of inter-locked mullite framework prepared by the TBA-based gel-casting process, Ceram. Int., 42 (2016), 15459–15463.

[7] S. Mey-Cloutier, C. Caliot, A. Kribus, Y. Gray, G. Flamant, Experimental study of ceramic foams used as high temperature volumetric solar absorber, Sol. Energy., 136 (2016), 226–235.

[8] E. C. Hammel, Q. L.-R. Ighodaro, O. I. Okoli, Processing and properties of advanced porous ceramics: An application based review, Ceram. Int., 40 (2014), 15351–15370.

[9] Z. Hou, H. Du, J. Liu, R. Hao, X. Dong, M. Liu, Fabrication and properties of mullite fiber matrix porous ceramics by a TBA-based gel-casting process, J. Eur. Ceram. Soc., 33 (2013), 717–725.

[10] L. Hu, C.-A. Wang, Y. Huang, Porous yttria-stabilized zirconia ceramics with ultra-low thermal conductivity, J. Mater. Sci., 45 (2010), 3242–3246.