Ceramic foams with highly open channel structure from direct foaming method in combination with hollow spheres as pore-former

Yu Zheng (✉ zhengyus@163.com)

Liaoning University of Science and Technology

Xudong Luo

University of Science and Technology Liaoning

Jiegang You

University of Science and Technology Liaoning

Zijun Peng

University of Science and Technology Liaoning

Shuhao Zhang

Tsinghua University

Rapid Communication

Keywords: Ceramic foams; Open channel; Direct foaming method; Hierarchical porous structure

Posted Date: May 28th, 2020

DOI: <https://doi.org/10.21203/rs.3.rs-31239/v1>

License: © ⓘ This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Version of Record: A version of this preprint was published at Journal of Asian Ceramic Societies on December 16th, 2020. See the published version at <https://doi.org/10.1080/21870764.2020.1847427>.

Abstract

To satisfy the ever-increasing demands for high-performance ceramic foams that could be applied in catalysts loader, filtrations and adsorptions, it is critical to develop technologies for ceramic foams with open channel structure. In this work, we fabricated ceramic foams with three-dimensional porous structure specially with open channels by combining direct foaming method with adding pore-forming agent method. There are two levels of length scale present in this hierarchically porous structure, that is, foam structure with spherical pores evolved from bubbles, and open pores on the cell wall derived from silica hollow spheres with thin shell as the pore-former. Hierarchical ZrO_2 based foams with porosity of 86.5%-95.1% and compressive strength of 2.05-5.67 MPa, and Al_2O_3 based foams with porosity of 86.2%-91.0% and compressive strength of 6.8-13.2 MPa were fabricated. The prepared ceramic foams characterized by this open channel structure are promising to perform outstandingly in the abovementioned fields due to their uniform pore size, low density as well as high mechanical strength.

1. Introduction

Owing to their excellent properties involving unique pore structure, low density, high specific surface area, outstanding specific strength as well as low thermal conductivity etc., ceramic foams are playing indispensable role in numerous fields as either structural or functional materials ^[1-2]. Therefore, it has become a research hotspot to develop novel porous materials with low cost, low bulk density and various microstructures to satisfy the ever-increasing application demands. From topological standpoint, porous ceramic materials can be categorized into closed pore structure and open pore structure. Closed pore structure usually endows porous materials with high strength and better thermal insulation property, while open pore structure promotes better permeability ^[3]. So far, direct foaming method, replica method and adding pore-forming agent method are mostly selected three methods for the preparation of porous materials ^[4-7]. As is well known, direct foaming method is featured by high-porosity level and closed pore structure, and usually chosen for the fields of thermal insulations and light-weight structural components ^[8]. In comparison to ceramic foams with closed pores, ceramic foams with open channel structure play important roles due to their high accessible specific surface area, and they are mainly applied in catalysis supports, selective separation, biomaterial engineering, etc., leading to more and more attention ^[9]. The replica method is one of the commonly employed routes to achieve highly open pores. A primary disadvantage of this technique is that the mechanical strength of the porous scaffolds is not favorable, as it is difficult to avoid the formation of microcracks in the struts during the template removal process ^[3]. Moreover, the burning out process of the polymer sponges would cause serious energy consumption and increase burden on the environment protection.

To meet the urgent requirements for multifunctionalities, the design and synthesis of hierarchically porous ceramics with three-dimensional porous frameworks and open channels become of great importance in recent years. In the current climate of sustainable development, we fabricated ceramic foams with hierarchically porous and open-channel structure by combining two methods in this study, i.

e., direct foaming method and adding pore-forming agent method. Firstly, colloidal ceramic foams containing particles and hollow spheres are prepared via direct foaming method, which would generate foam structure. And hollow spheres serving as pore-former could favor forming secondary pores of open windows on the cell wall. Such a strategy employing bubbles as foam template and hollow spheres as pore-former offers several advantages, such as high porosity level, ordered pore structure, free of binder removal step, environmental friendliness and high specific strength. Both ZrO_2 and Al_2O_3 based ceramic foams with hierarchical open pores are obtained, and their microstructure as well as mechanical strength are investigated.

2. Experiment And Characterization

Materials

In this study, ZrO_2 particles with average particle size of 0.48 μm and boehmite nanoparticles with average particle size below 100 nm were employed to prepare ZrO_2 based foams and Al_2O_3 based foams, which were provided from Guangdong Orient Zirconia Co., Ltd., China, and Hangzhou Zhihua Technology Co., Ltd., China, respectively. Silica hollow spheres with diameter of 5-80 μm were commercially purchased from Forsman Scientific (Beijing) Co., Ltd., China. Long-chain surfactant sodium dodecyl sulfate (abbreviated to SDS) which was employed as foaming agent, was purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Agar was also purchased from Sinopharm Chemical Reagent Co., Ltd., China. The pH of colloidal suspension was tailored via 2 mol/L HCl solution.

Preparation

In the case of ZrO_2 based foams, homogeneously colloidal suspension containing ZrO_2 particles and deionized water was prepared via ball milling for 4 h. The suspension with pH of 7.0 was heated in 80°C water bath, followed by adding hot concentrated agar solution with temperature of 80°C. Then, SDS was added into the above suspension, followed by frothing via mechanical stirring with high speed of 2000 rpm. During mechanical stirring, silica hollow spheres were added little by little. The concentration of ZrO_2 particles, silica hollow spheres, agar and SDS in the final suspension were 30 wt%, 6 wt%, 1 wt%, 0.05 wt%, respectively. The foamed suspension was cooled down firstly with temperature of 2°C for 5 mins, and then dried at room temperature.

In the case of Al_2O_3 based ceramic foams, homogeneously colloidal suspension containing 30 wt% boehmite nanoparticles and deionized water was prepared by mixing them under 80°C water bath for 24 h. Subsequently, SDS was added followed by mechanical stirring in room temperature with high speed of 2000 rpm. During mechanical stirring, sieved silica hollow spheres (with final concentration of 6 wt%, size smaller than 20 μm) were added little by little, and then HCl solution was added drop by drop, which decreased pH below 4.0 to promote the gelation of boehmite foams. The obtained foams were dried in a humidity chamber with temperature of 30°C and humidity of 90%. Both dried Al_2O_3 based foams and ZrO_2 based foams were sintered in a furnace with a heating rate of 3°C /min and a dwelling time of 2 h.

Characterization

The apparent densities were calculated by the ratio between mass and dimensions of machined specimens. Total porosity was calculated according to equation , where P is the total porosity, and D_b are the true density and bulk density of ceramic foams, respectively. The microstructure of ZrO_2 based foams and Al_2O_3 based foams was observed by scanning electron microscope (SEM, MERLIN VP Compact, Carl Zeiss, Jena, Germany). The compressive strength was measured using a universal material testing machine (AG-IC 20 kN, Shimadzu, Japan) with loading speed of 1 mm/min, and at least three specimens with cubic shape and dimensions in the range of 10-20 mm were measured to calculate average values.

3. Results And Discussion

As illustrated in Fig. 1, the foams are subjected to solidification with the assistance of agar molecules in the case of ZrO_2 based foams ^[11], and rapid gelation of boehmite nanoparticles was triggered by decreasing pH in the case of Al_2O_3 based foams ^[12]. Therefore, the dried foams exhibit favorable strength, that keep the whole porous green body holding together and be free of breaking. The hollow spheres exhibit excellent spherical morphology, large-volume cavity, very thin shell and low softening temperature. It is found that these spheres melt when sintering temperature increases to around 1000°C, which is much lower than that of Al_2O_3 and ZrO_2 . In the direct foaming process, close assembly of particles at water/air interfaces would cause the mostly closed pores after sintering ^[13]. By contrast, hollow spheres inserting in the cell wall would occupy the space firstly, exactly acting as pore former, and thus facilitate the achievement of open windows on the cell wall after their melting during heat treatment process.

As shown in Fig. 2, the formation of open windows on the cell wall of ZrO_2 foams sintered above 1000°C leads to the interconnection of pores. The obtained ZrO_2 based foams exhibit hierarchically porous structure in two levels of length scale, that is, spherical pores evolved from frothed bubbles, the pore diameter of which are in the range of 100-300 μm and open windows on the cell wall with diameter around 20-80 μm , which are derived from the hollow spheres. Such a strategy combines the advantage of direct foaming method and adding pore-forming agent method, and consequently endows the obtained ZrO_2 based foams with high porosity level, uniform pore size and open channel structure, further contributing to the enhancement of strength. These features render ceramic foams with an easy penetration of gas or liquid, which expands their application as functional materials in a broad range of specific hi-tech fields, including catalytic loader, filtration and adsorption, etc.

As can be seen from Fig. 3(a), in addition to m- ZrO_2 , ZrSiO_4 and very small amount of stishovite are detected in the ZrO_2 based foams. Fig. 3(b) demonstrates the compressive strength of ZrO_2 based foams prepared at different sintering temperatures. Highly porous ZrO_2 based foams with porosity ranging from 86.5% to 95.1% are synthesized in this work, which possessing compressive strength of 2.05-5.67 MPa.

The shrinkage, porosity and strength of ZrO_2 based foams can be controlled by sintering temperature. It is noted that high sintering temperature above 1400°C is normally needed for ZrO_2 ceramics to realize densification of grains and high strength ^[14-15], while the foams reported here sintered at 1000°C still display excellent mechanical strength, up to around 2 MPa. This value is very similar to pure ZrO_2 ceramic foams prepared with only ZrO_2 particles, which possesses porosity of 95.4% and compressive strength of 2.1 MPa ^[15]. The achievement of both low sintering temperature and high strength is attributed to the silica hollow spheres with thin shell and low sintering temperature that would melt and fill in the space among insufficiently sintered ZrO_2 grains, acting as high-temperature binder, and therefore contributing to the formation of dense wall without gaps between grains, as can be seen clearly in Fig. 2(b).

In addition to ZrO_2 based foams, we also demonstrate the fabrication of Al_2O_3 based foams with open channel via the approach illustrated in Fig. 1(b). Similar structure is observed, as shown in Fig. 4(a-d). After sintering, boehmite would transform to Al_2O_3 via losing bound water and hydroxyl groups ^[13]. It is demonstrated that Al_2O_3 based foams with pore size of 20-80 μm together with open windows with diameter around 3-10 μm have been obtained by this route. The obtained Al_2O_3 based foams contain α - Al_2O_3 , Al_2SiO_5 , α -tridymite and small amount of cristobalite, as shown in Fig. 4(e). By adjusting SDS concentration, Al_2O_3 based ceramic foams exhibit porosity in the range of 86.2%-91.0% and compressive strength ranging from 13.2 MPa to 6.8 MPa (see Fig. 4(f)). Therefore, the combination of direct foaming method and inorganic hollow spheres with low melting point as pore-former is a universal and feasible approach to fabricate ceramic foams with open pores. Such a strategy is featured by no discharge of hazardous substances, low energy consumption due to low sintering temperature, which is a promising and eco-friendly approach for the fabrication of ceramic foams with open channels, low density, and uniform pore size.

4. Conclusions

A simple, versatile, low-cost and eco-friendly approach has been proposed to fabricate ceramic foams with hierarchically porous structure as well as open channels. The overall three-dimensional porous structure was built by employing bubbles as templates, which is benefited from the direct foaming method and contributes to the uniform pore distribution. Both ZrO_2 and Al_2O_3 based foams are fabricated based on the gelation of foams, which could be achieved by temperature-transformation of agar-included suspension or pH-initiated gelation of boehmite nanoparticles, respectively. The secondary pores were designed via selecting silica hollow spheres as pore-former. Hollow spheres with low melting point, thin shell wall, high volume cavity enable the formation of open windows during sintering process. The prepared ZrO_2 and Al_2O_3 based foams with three-dimensional porous skeleton and interconnected pores behaves low bulk density and relatively high compressive strength, enlarging their potential applications in the fields of gas/liquid filtrations, lightweight structural components, catalyst supports and the like.

Declarations

Acknowledgments

We are grateful for the financially support from the National Natural Science Foundation of China (Grant No. 51772139).

References

- [1] T. Ohji, M. Fukushima. Macro-porous ceramics: processing and properties. *Int. Mater. Rev.* 57 (2012) 115-131.
- [2] W. L. Huo, Y. G. Chen, Z. J. Zhang, J. J. Liu, S. Yan, J.M. Wu, X. Y. Zhang, J. L. Yang. Highly porous barium strontium titanate (BST) ceramic foams with low dielectric constant from particle-stabilized foams. *J. Am. Ceram. Soc.* 101(2018) 1737-1746.
- [3] A. R. Studart, U. T. Gonzenbach, E. Tervoort, L. J. Gauckler. Processing Routes to Macroporous Ceramics: A Review. *J. Am. Ceram. Soc.* 89 (2006) 1771-1789.
- [4] P. Colombo. Conventional and novel processing methods for cellular ceramics. *Philos Trans A Math Phys Eng. Sci.* 364(2006)109-124.
- [5] U.T. Gonzenbach, A.R. Studart, E. Tervoort, L.J. Gauckler. Macroporous ceramics from particle-stabilized wet foams. *J. Am. Ceram. Soc.* 90 (2010) 16-22.
- [6] A. A. M. N. Mohd, C. H. Lee, A. A. Zainal. Preparation and characterization of ceramic foam produced via polymeric foam replication method. *J. Mater. Proc. Technol.* 207(2008) 235-239.
- [7] S. Li, C. A. Wang, J. Zhou. Effect of starch addition on microstructure and properties of highly porous alumina ceramics. *Ceram. Int.* 39(2013): 8833-8839.
- [8] B. P. Binks. Particles as surfactants-similarities and differences. *Curr. Opin. Colloid Interface Sci.* 7 (2002) 21-41.
- [9] Y. Zhou, M. Antonietti. A novel tailored bimodal porous silica with well-defined inverse opal microstructure and super-microporous lamellar nanostructure. *Chem. Commun.* 20(2003) 2564-2565.
- [10] W. L. Huo, Y. G. Chen, J. L. Yang, Y. Huang. Enhancement of ultra-light alumina dried foams from particle-stabilized foams with Assistance of Agar and PVA. *Int. J. Appl. Ceram. Tec.* 14(2017) 928–937.
- [11] Y. G. Chen, W. L. Huo, X. Y. Zhang, Y. J. Lu, S. Yan, J.J. Liu, K. Gan, J. L. Yang. Ultrahigh-Strength Alumina Ceramic Foams via Gelation of Foamed Boehmite Sol. *J. Am. Ceram. Soc.* 12(2019) 5503-5513.

[12] W. L. Huo, X. Y. Zhang, S. Y. Hou, Y. G. Chen, Y. L. Wang, J. L. Yang. Aerogel-like Ceramic Foams with Super-high Porosity and Nanoscale Cell Wall from Sol Nanoparticles Stabilized Foams. *J. Am. Ceram. Soc.* 102(2019) 3753–3762.

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

[14] J. J. Sun, Z. J. Hu, J. N. Li, H. B. Zhang, C. C. Sun. Thermal and mechanical properties of fibrous zirconia ceramics with ultra-high porosity. *Ceram. Int.* 40(2014) 11787-11793.

[15] W. L. Huo, X. Y. Zhang, K. Gan, D. Wang, Y. G. Chen, J. L. Yang. Mechanical strength of highly porous ceramic foams with thin and lamellate cell wall from particle-stabilized foams. *Ceram. Int.* 44(2018) 5780-5784.

Figures

Figure 1

Preparation schematics of ZrO₂ based foams (a), and Al₂O₃ based foams (b)

Figure 2

SEM images of ZrO₂ based foams prepared at 1000°C (a,b), 1500°C (c,d), and 1550°C (e,f)

Figure 3

(a) XRD patterns and (b) Linear shrinkage, porosity and compressive strength of ZrO₂ based ceramic foams with open channel structure

Figure 4

SEM images of Al₂O₃ based foams sintered at 1250°C (a,b), 1300°C (c,d), XRD patterns of Al₂O₃ based foams sintered at 1300°C(e), porosity and strength of Al₂O₃ based foams tailored by SDS concentration (e).