

Fabrication of Macroporous Ceramics with Trimodal Pore Structure

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Abstract. This research reported the successful fabrication of highly porous ceramic materials with hierarchical structure by using a foaming and agar gelation method. Formations of macropores caused by foaming, window pores that pores are connected each other, and micropores caused by agar were confirmed through the present study. The sizes of macropores and window pores decreased with the increase in agar contents. The results are likely due to the fact that the sizes of pores remained more or less constant due to the stabilized bubbles generated through a fast gelation at low temperature. Based on the results from this study, it is suggested that the control of pore structure could be possible by adjusting the level of agar contents.

Keywords: porous ceramic materials, hierarchical structure, agar gelation

1. Introduction

Porous materials have been widely used in applications, such as molten metal filtration, thermal insulators, hot gas filtration, bioceramic, and catalyst support, where fluid transport is required [1,2]. Especially, ceramic foams have gained interest in recent years due to their potential applications as carriers since they possess superior properties such as high gas permeability, high specific surface area enhancing mass transfer, as well as the radial mixing in the network structure. With this attractive property, it is applied to the industries like filters, waste and exhaust gas/water purification [2-4].

There are largely two distinguished production of porous ceramics. One method is the polymeric sponge replica, in which a polymeric sponge impregnated with a slurry is sintered [5,6]. The second technique is direct foaming, in which a ceramic slurry containing organic monomers is foamed and solidified by polymerization of the organic gelling agents [5,7]. Highly porous ceramic foams have been improved by the foaming and gelcasting process. As there is fast solidification by in situ polymerization of water soluble monomers with the gelling agent included in the foamed slurry, it gains the high gel strength of porous structure. As a result, it forms the high interconnected porous network in sphere shape [4,7]. The biggest disadvantage in this gelcasting process is the generally toxic acrylamide of gelling agent that is in frequent use. Therefore, recently there are many studies applying non-toxic biopolymer to replace gelcasting reagent. [8]. Among all, agar solution has high gel strength at low temperature as well as fast gelation, so that it is possibly used as a gelcasting reagent [9].

Ceramic foams vary the property by pore structure. The pore structure is commonly divided into pore morphology, porosity and pore size. The pore morphology is then divided into open and closed pores. In case of open pore, it is distinguished into penetrating pore which fluid can penetrate and the non-penetrating pore that is also called as ink-bottle pore. Open pore is the very important factor of the filter with the property of separation-filtration and the closed pore contributes to the properties of light-weight material and heat

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insulating material [10]. The pore size of macropores has the property required as a filter with easy fluid flow [4,9], and the micropores increases the specific surface area that is useful for water/air purification [11] and catalytic support [12]. Therefore, if the monolithic matrix which has the combined structure of different pore sizes as well as excellent open pore morphology is possible, it will get the expanded property on top of ceramic foams and it will be applicable as a spot-lighted material in the environmental industry [13,14]. Recently, there are many studies on hierarchical monolith production with bi-modal or tri-modal pore structure [13,14]. Here, we present the preparation and characterization of highly porous ceramic composites in the form of monoliths having tri-modal pore systems (small-sized macro-, pore window and large-sized macroporous). The monoliths have been fabricated by using direct foaming from alumina slurry and agar gelation. We measured the microstructure of the produced sample according to the agar additive concentration and evaluated each pore size by the range.

2. Materials and Methods

2.1. Preparation processing

The ceramic powder investigated was a commercially available alumina powder (A34, NLM Co., Japan) with a specific surface area of 3.8 m²/g and a mean particle size of 3 μm. The stable agar (MSA Co., Korea) was used as gelling agent. The concentration of alumina slurry was 50 vol.%, and polyacrylic acid (PAA), a dispersing agent, was added to slurry with a concentration of 0.8wt.% slurry. Homogenization of alumina slurry was carried out by mechanical mixing, followed by attrition milling for 1 h at 500 rpm using alumina ball and jar. Sodium lauryl sulfate (SLS) supplied by Sigma-Aldrich was added to the slurry in order to make a ceramic foam. First, in a typical preparation, an aqueous gelcasting-suspension containing 2, 3, 4 and 6 g of agar powder in 100 mL of distilled water (2, 3, 4 and 6 in weight) was heated for 3 min at 70 °C. And then, in order to make foamed slurry, 2.8×10⁻³ M of SLS was added to a 200 cm³ of alumina slurry which had a 50 vol.% concentration and were kept at 60 °C. The foamed suspensions were whisked vigorously in order to swell to 800 cm³. The temperature was maintained as 60 °C. The final mixture suspension was placed into the mold, left in the 10 °C refrigerator for 24 h. The gelled sample was separated from mold, followed by drying in air at room temperature for 24 h. Sintering of the sample in zirconia crucible was performed with an electric furnace at 1550 °C for 2 h using heating rate of 100 °C/h up to 600 °C and then 150 °C/h up to the final temperature in air.

2.2. Characterization

The average particle size and the particle size distribution of used agar were measured by using particle size analyzer (SALD-2001, Shimadzu, Japan). The viscosity of alumina suspension with agar was measured at various temperatures with a digital rotation viscometer (LVDV-11+P, Brookfield, USA). The bulk density to measure the total porosity of the produced sample was acquired by regular sized production. The true density of alumina powder (3.98 g/cm³) and the apparent density of the produced sample (n≥50) were measured by using Helium pycnometer (Accupyc 1340, Micromeritics, USA) and then used to calculate open porosity and closed porosity [10]. FE-SEM (JSM-6300, JEOL, Japan) was used to understand the surface morphology and microstructure of the porous sample.

3. Results and Discussion

The 800 cm³ of 50 vol.% alumina foam slurry was mixed with agar solution(2, 3, 4 and 6 wt.%) of 100cm³ and the temperature was maintained at 60 °C. The final alumina content was always fixed at 34 vol.% (67 wt.%) in order to determine the effect of agar concentration on viscosity of the ceramic slurry. The total concentration of agar as gelling matter in final slurries was 0.50, 0.75, 1.00 and 1.50 wt.% with regard to dry alumina. The continuous viscosity measurement was performed by heating the agar added slurry temperature from 25 °C to 70°C then cooled back to 15 °C. The reason why 70 °C was the temperature turning point was because it was reported that the viscosity of agar solution by temperature had its maximum between 65 °C and 90 °C, and 80 °C was reported to be the maximum melting point [15]. Therefore, the temperature turning point was set as 70 °C when measuring the slurry viscosity change by temperature.

Fig. 1 describes the measurement of viscosity for each temperature of alumina slurry by agar concentration. As there was more agar additive amount, there was higher viscosity and the viscosity increased from the temperature of around 55 °C when heated. Moreover, it is seen that the viscosity of agar added slurry increased up to 70 °C. Later, as there was cooling down of slurry, the viscosity largely increased and the increase occurred as there was higher agar additive. Particularly, the slurry with 1.50 wt.% additive rapidly increased its viscosity at around the temperature of 25 °C. Therefore, the slurry viscosity became high as higher amount of agar was added. In addition, greater viscosity change was observed when it cooled.

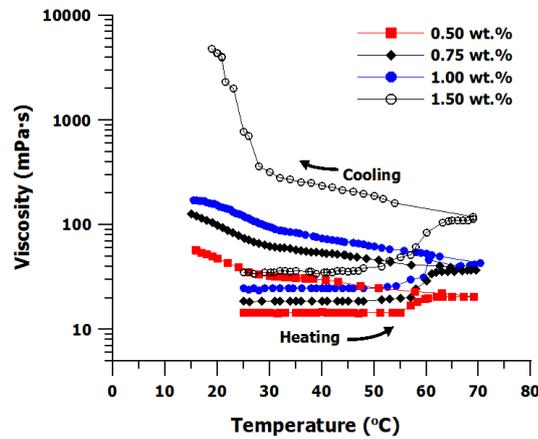


Fig. 1 Continuous variation of viscosity of alumina suspensions with the fixed solids loading of 34 vol.% and varied agar contents.

The microstructure picture using SEM for the agar added samples is described in Fig. 2. As shown in Fig. 2(a), the sample has large-sized pores and medium-sized windows connecting pore to pore. In general, it was possible to form macropores and windows during the foaming process [2,4]. As such, formation of macropores and windows are considered to have taken place in the present study. The smallest micropores of the sample were set as pores formed in the sample structure and shown in Fig. 2(b). The sample manufactured through the foaming process and added with agar confirmed that there are large sized pore and window as well as micropore inside the structure. Particularly, the size of the most pores formed inside the structure was 2 μm or less and they were numerous distributed as shown in Fig. 2(b). Fig. 2(c) and Fig. 2(d) are microstructure picture of samples with a 0.50 wt.% and a 1.50 wt.% of agar concentration, respectively. It was seen that the two pictures with different agar concentrations have different pore sizes and it is thought that relatively larger pores were formed when lower agar concentration was used.

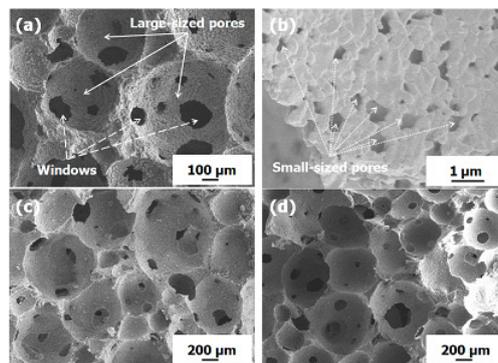


Fig. 2 SEM micrographs of sintered sample consist of: (a) large-sized pores and windows and (b) small-sized pores. (c) and (d) show the microstructure of the samples prepared with 0.50 wt.% and a 1.50 wt.% of agar concentration.

Table 1 describes the structural property of different agar additive samples. As there is more agar additive, the total porosity was reduced a little but the open porosity increased. The micropore size formed inside the structure of the sample produced in this research was impossible to measure separately, so that it

was calculated by using total porosity. The total porosity according to the size of the sample was set to be composed of macropore porosity (ϵ_{macro} , $d_p \geq 10 \mu\text{m}$) and micropore porosity (ϵ_{micro} , $d_p \leq 2\mu\text{m}$). Strut porosity (ϵ_{strut}) of the sample which does not proceed foaming in the manufacturing process was measured to calculate the following formula [16].

$$\epsilon_{\text{macro}} = (\epsilon_t - \epsilon_{\text{strut}}) / (1 - \epsilon_{\text{strut}})$$

$$\epsilon_{\text{micro}} = \epsilon_t - \epsilon_{\text{macro}}$$

Here, ϵ_t represents total porosity of ceramic foams. The structural property of sample by agar additive is described in Table 1. As macroporosity decreased in accordance with the increasing agar contents, microporosity increased. In addition, Table 1 shows average size of large pores. The large-sized pores of the samples were measured from the images ($n \geq 50$) taken from a scanning electron microscopy (FE-SEM, JSM-6300, JEOL Co., Japan) using an image analysis system (KH-7700, HIROX Co., Japan). The average large pore size was 590, 528, 486 and 344 μm when agar additive was 0.50, 0.75, 1.00 and 1.50 wt.%, respectively. The average large pore size was small in the sample with higher agar additive.

Table 1 Textural properties of sintered sample

Agar contents (wt.%)	Total porosity (%)	Open porosity (%)	Closed porosity (%)	Macro porosity (%)	Micro porosity (%)	Average pore size (μm)
0.50	90.5±2.2	82.2±10.3	8.2±9.5	81.2±0.9	9.2±0.9	590
0.75	89.9±5.5	80.4±9.7	10.1±12.7	80.0±0.3	10.0±0.3	528
1.00	89.5±0.8	80.3±4.7	9.1±4.9	78.7±0.9	11.1±0.9	486
1.50	88.4±1.1	83.1±2.8	6.9±3.4	75.8±0.1	12.5±0.1	344

Above results may be connected with the outcomes of Fig. 2. The porosity deviation was confirmed to be larger in case of low-level agar contents compared with that of high-level agar contents. It is considered that there is maintenance of relatively consistent small sized, stable size distribution of pore formation inside the slurry due to the rapid viscosity increase at the low temperature when there is high agar additive amount. Therefore, it is considered that the pore structure control is possible with agar additive when producing porous ceramic materials that are developed in this research.

4. Conclusions

This research produced highly porous ceramics with tri-modal pore structure by using foaming and agar gelation and acquired following results. First, there was rapid slurry viscosity change as there is more agar additive and the viscosity largely increased at around the temperature of 25 °C in the process of cooling from the temperature at 70 °C. Second, it encouraged the large pore and window pore formation by foaming and eased the formation of micropore with agar additive. However, the large pore size decreased as more agars were added. It is thought that there is pore stabilization by rapid gelation with greater agar additive. Third, it was measured that the microporosity of 12.5±0.1% and average large pore size of 344 μm from the sample with the agar additive of 1.50 wt.%. With these results, it was possible to perform monolith production with hierarchical structure (small macro-, window pore, and large-sized pore) using foaming and gelation, and it is also considered that the pore structure adjustment is possible by the agar additive concentration.

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6. References

- [1] P. Sepulveda. Gelcasting foams for porous ceramics. *Am. Ceram. Soc. Bul.* 1997, **76** (10): 61-65.
- [2] M. Scheffler, and P. Colombo. *Cellular ceramics: structure, manufacturing, properties and applications*. Wiley-VCH, UK, 2005.
- [3] G. Saracco, and L. Montanaro. Catalytic ceramic filters for flue gas cleaning. 1. preparation and characterization. *Ind. Eng. Chem. Res.* 1995, **34**: 1471-1479.
- [4] J. Park, J. Lee, and S. Lee. Preparation of porous cordierite using gelcasting method and its feasibility as a filter. *J. Porous Mater.* 2002, **9**: 203-210.
- [5] J. Saggio-Woyansky, C.E. Scott, and W. Minnear. Processing of porous ceramics. *Am. Ceram. Soc. Bul.* 1992, **71**: 1674-1682.
- [6] E. de Sousa, C.R. Rambo, D. Hotza A.P. Novaes de Oliveira, T. Fey, and P. Greil. Microstructure and properties of LZSA glass-ceramic foams. *Mater. Sci. Eng. A.* 2008, **476**: 89-97.
- [7] P. Sepulveda, and J.G.P. Binner. Processing of cellular ceramics by foaming and in situ polymerization of organic monomers. *J. Eur. Ceram. Soc.* 1999, **19**: 2059-2066.
- [8] M. Bengisu, and E. Yilmaz. Gelcasting of alumina and zirconia using chitosan gels. *Ceram. Inter.* 2002, **28**: 431-438.
- [9] R. Mouazer, I. Thijs, S. Mullens, and J. Luyten. SiC foams produced by gelcasting: synthesis and characterization. *Adv. Eng. Mater.* 2004, **6**: 340-343.
- [10] K. Ishizaki, S. Komarneni, and M. Nanko, *Porous materials: process technology and applications*, Kluwer Academic Publishers, London, 1998.
- [11] H. Kim, S. Lee, Y. Han, and J. Park. Preparation of dip-coated TiO₂ photocatalyst on ceramic foam pellets. *J. Mater. Sci.* 2006, **46**: 6615-6253.
- [12] S. Furuta, H. Katsuki, and S. Komarneni. Modification of porous silica with activated carbon and its application for fixation of yeasts. *J. Porous Mater.* 2001, **8**: 43-48.
- [13] H. Maekawa, J. Esquena, S. Bishop, C. Solans, and B.F. Chmelka. Meso/macroporous inorganic oxide monoliths from polymer foams. *Adv. Mater.*, 2003, **15**: 591-596.
- [14] L. Huerta, J.E. Haskouri, D. Vie, M. Comes, J. Latorre, C. Guillem, M.D. Marcos, R. Martinez-Manez, A. Beltran, D. Beltran, and P. Amoros. Nanosized mesoporous silica coatings on ceramic foams: new hierarchical rigid monoliths. *Chem. Mater.* 2007, **19**: 1082-1088.
- [15] A.J. Millan, R. Moreno, and M.I. Nieto. Thermogelling polysaccharides for aqueous gelcasting-part I: a comparative study of gelling additives. *J. Eur. Ceram. Soc.* 2002, **22**: 2209-2215.
- [16] J. Lee, and J. Park. Processing of porous ceramics spheres by pseudo double-emulsion method. *Ceram. Inter.* 2003, **29**: 271-278.