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Gelcasting fabrication of porous ceramics using a continuous process

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Abstract

A continuous process for gelcasting fabrication of porous ceramics is reported. The key characteristic of this method is the mixing of slurry and N_2 bubbles, formed from a separated canister containing a surfactant prior to foaming of slurry, in a spiral mixer. The microstructure of the resulting porous ceramic is compared with that of sample fabricated by the conventional discontinuous process with N_2-gas controlling system. Porous ceramic produced using the new method displays lower density, higher open and total porosities, and broad pore size distribution. The obtained porous ceramics by the two routes are further investigated by sound absorption and heat insulation tests. Porous ceramic produced using the new method shows higher value of sound absorption coefficients, which suggests that the large porosity augment the sound absorbing performance of ceramics sample. The pore structure could also affect the thermal conductivity of the porous ceramics. With high porosity, sample fabricated with new method displayed lower thermal conductivity.

Keyword: Gelcasting; Porosity; Thermal conductivity; Structural applications

1. Introduction

The incorporation of porosity within a tailored structure gives porous ceramics many intrinsic properties such as high permeability, high surface area, and good insulating characteristics. Porous ceramics have found a wide variety of applications including as filters, membranes, sensors, catalyst carriers, piezoelectric ceramics, biomedical and construction materials.[1] The microstructure such as porosity and pore size distribution are very important factors for many potential applications of porous ceramics. For instance, the increase in porosity of porous ceramic caused an increase in the permeability and the ideal combination of pore size and porosity could optimize the relationship of permeability and mechanical strength.[2] Porous ceramics with different porous morphology and size distribution can be fabricated by different routes, such as (i) burning out a polymeric sponge impregnated with a ceramic slurry,[3] (ii) solid-state sintering,[4] (iii) sol–gel process,[5] (iv) replication of polymer foams by impregnation,[6] and gelcasting process.[1,2,7–12] Among them, gelcasting is a new processing route for the fabrication of highly porous ceramics. This method, originally developed by Oak Ridge national laboratory for the fabrication of dense ceramics,[13] combines the foaming of aqueous slurry of ceramic powder and organic monomers and the in situ polymerization of the foamed slurry. In a traditional foaming procedure, foams can be produced by mechanical frothing in an N_2 controlling system. After formation of foams, the slurry is rapidly gelled in the N_2 controlling system by means of polymerization of the monomers. A surfactant is necessary for the stabilization of the foams for a longer time prior to solidification by reducing the surface tension of the gas-liquid interfaces. Sepulveda et al. reported that several transformations in the bubble structure might occur within the interval between foam generation and foam solidification.[12] Some bubbles may shrink and disappear whilst others may coalesce to form large bubbles. So, the changes in the foam structure prior to solidification are important because they influence the final cell size distribution, wall thickness and microstructure of the solid foams. On the other hand, the atmosphere types containing O_2 were revealed to be improper for gelcasting since the formation of strong binder networks by the in situ polymerization of monomers failed in the surface regions.[14] Several alternative gelling agents have been developed for

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the elimination of the surface spallation of green bodies due to the exposure to air.[9,15–17]

Here, we report a new method for the gelcasting fabrication of porous ceramics developed in our laboratory. This method is the mixing of slurry and N_2 bubbles, formed from a separated canister containing a surfactant prior to foaming of slurry, in a spiral mixer. The microstructure properties of the porous ceramic using the new method are compared with that prepared using the conventional method. On the other hand, our former investigation had shown that the porous ceramics fabricated by gelcasting using waste resources has great potential for the use as light ceramic tile with high mechanical strength.[9,10] Developing a porous ceramics as outside construction materials will provide the ceramic tile not only lightness but also other functions such as insulation, machinability and sound absorbability. In this study, the sound absorption and heat insulation properties of the porous ceramics fabricated by the new method are further investigated and compared with that prepared using the conventional method.

2. Experimental procedure

2.1. Materials

Industrial and mining wastes such as glass bottles and low-grade silica and alumina were used as raw materials after grinding up to about 15 μm. Monofunctional methacrylamide (MMA) and difunctional *N*,*N*′-methylenbisacrylamide (MBAM) were used as monomers. To initiate and accelerate gelation of the monomers, ammonium persulfate (APS) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TEMED) were used as initiator and catalyst, respectively. Ammonium lauryl sulfate was used as a surfactant and ammonium citrate as a dispersant.

2.2. Procedure

A flow chart of the conventional gelcasting process has been given in some literatures.[1,9,10,12] Slurry with a waste concentration of 68% was prepared by ball-milling. Then, foaming of slurry was conducted by mechanical stirring of the slurry with assistance of the surfactant. This procedure was performed in a sealed chamber under a controlled N_2 atmosphere. After addition of initiator and catalyst, the foamed slurry was poured into a plastic mold for in situ solidification. The wet gelled sample was then de-molded, dried at 25 °C in a controlled-humidity drying chamber for 5 days. Sintering was carried out at 1000 °C for 3 h. The composition of the slurry is summarized in Table 1.

For the new gelcasting process, a spiral mixer (Fig. 1) was used to foam the slurry. N_2 bubbles were formed from a separated canister containing a surfactant prior to foaming of slurry. The atmosphere in the space between the stator and the rotor was firstly charged with N_2 bubbles. Subsequently, ball-milled slurry with initiator, catalyst and N_2 bubbles were simultaneously added to the spiral mixer rotating at 3000 rpm. The resulting slurry was removed from the mixer and poured into a plastic mold for in situ solidification. The drying and sintering procedures are the same as those for the conventional method. The slurry flux was 50 ml/min, surfactant flux 3 ml/min, and N_2 bubble flux 50 ml/min. The component contents of the slurry system were identical in both methods.

Table 1
Composition of the slurry for gelcasting

Substance	Amount (g)
Wastes	680.00
Distilled water	239.66
Monomer	63.91
Cross-linker	15.98
Initiator	0.22
Catalyst	0.22
Dispersant	0.61
Surfactant	1.65[a]

[a] ml.

2.3. Characterization

The density, open and total porosities of the sintered samples were determined by Archmede's method. The theoretical density of fully densified ceramic (2.68 g/cm^3) was used as a reference to calculate the relative porosity. The average pore and pore size distribution were obtained by using Image-Pro Plus 4.5 (Planetron Inc.), following the microscopy observations performed under Eclipse E600 POL (Nikon).

Sound absorption was measured by vertical incidence sound absorption device (two-microphone impedance measurement tube, BK4206A, Brüel&Kjær). The sound absorption performance of the ceramics is defined by the sound absorption coefficient (α), which is the ratio of the unreflected sound intensity at the surface to the incident sound intensity.[18] The sound absorption coefficient (α) can be calculated using

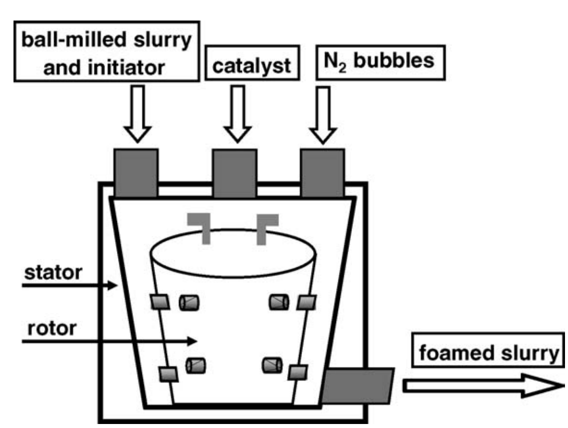

Fig. 1. Schematic representation of experiment apparatus for fabrication of porous ceramics.

the following relationships:

$$\alpha = 1 - \left[\frac{n-1}{n+1}\right]^2$$

$$n = \frac{P_{MAX}}{P_{MIN}}$$

where n is the standing wave ratio, and P_{MAX} and P_{MIN} are the maximum and minimum sound pressures in the impedance tube.

Heat conductivity was obtained by a quick thermometer (QTM-type-500, Kyoto Electronics Manufacturing).

3. Results and discussion

3.1. Fabrication and microstructure of porous ceramics

Generally, gelcasting is based on the combination of the foaming of aqueous slurry and the in situ polymerization of the foamed slurry. The foaming method has an important effect on the properties of the foamed slurry and will affect the pore structure and intrinsic properties of the porous ceramics. The difference between the conventional discontinuous process and our new process is the different method of foaming the slurry. For the conventional process, a N_2 controlling system is necessary. The bubbles are introduced into slurry by vigorous stirring under the N_2 atmosphere. For the new process, N_2 bubbles are produced from a separated canister containing a surfactant prior to foaming of slurry. Subsequently, rapid mixing of unfoamed slurry and N_2 bubbles takes place in a spiral mixer. The spiral mixer consists of a cylindrical rotor with total 22 pins on the surface and a stator with a gap of 5 cm between them. The ball-milled slurry with initiator, catalyst and N_2 bubbles were simultaneously mixed in the gap between the rotor and stator. The component contents of the slurry system and the drying and sintering procedures are the same as those for the conventional method.

The pore parameters of the porous ceramic fabricated by the two methods are listed in Table 2. The density of the porous ceramic fabricated by the new method is lower than that porous ceramic fabricated by the conventional method, which indicates the formation of large volume pores for the former sample. As expected, the porous ceramic fabricated by the new method shows a higher total porosity. Fig. 2 shows optical photographs of porous ceramics fabricated by the different process, which provide information about pore morphology and pore size. For the porous ceramic fabricated by the new method most pores are interconnected with others causing opened pores. The thickness of struts between pores in the structure of the sample is thinner than that of sample fabricated by the conventional method. The pore morphology leads to the former sample with a larger open and total porosities. Additionally, a large number of the pores in the former sample are in a range from several to a few hundred micrometers in diameter. However, the pore size in porous ceramic fabricated by the conventional method shows a more uniform distribution. The pore size distributions of the two samples, obtained by using image analysis, are illustrated in Fig. 3. The sample fabricated using the conventional method shows sharp double-peak around 100 μm. The relative height of the peak displays the extent of pores with the similar size. On the other hand, for the sample fabricated using the new method, four main wider peaks appear at 90, 140, 240 and 340 μm.

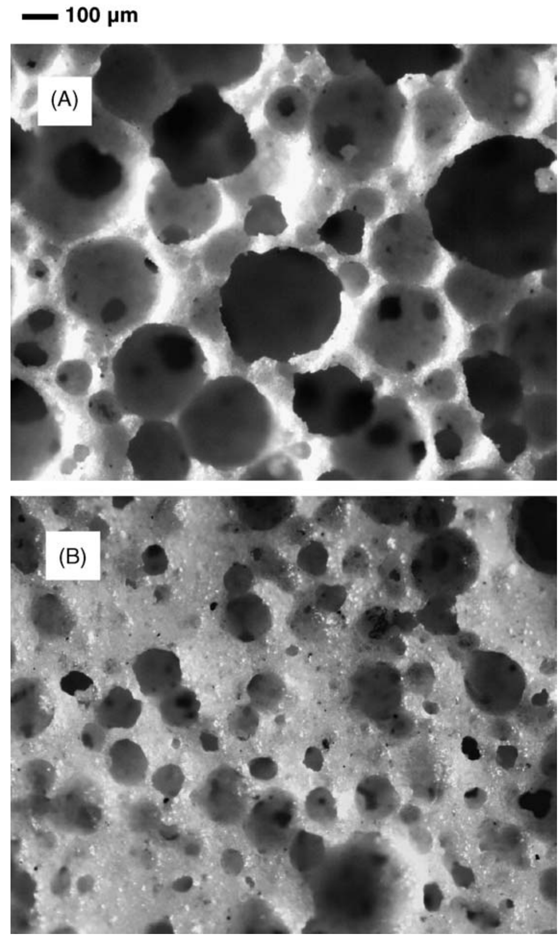

Fig. 2. Optical photographs of porous ceramics fabricated by the new method (A) and the conventional method (B).

Table 2
Microstructure parameters and thermal conductivity of the porous ceramics fabricated by the two different methods

Samples	Final density (g/cm^3)	Open porosity (%)	Total porosity (%)	Mean pore dimension (μm)	Thermal conductivity (W/mK)
New method	0.696	68.3	73.5	216.9	0.23
Conventional method	0.736	53.4	64.7	116.4	0.45

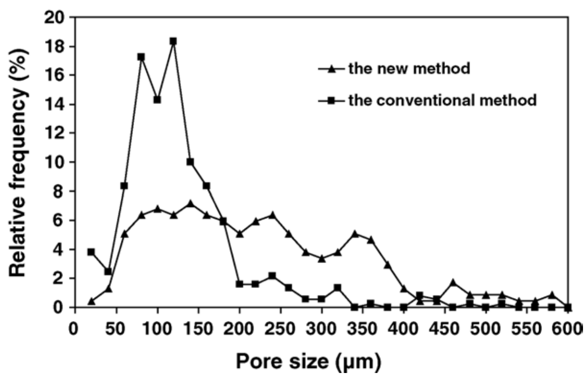

Fig. 3. Pore size distribution of porous ceramics fabricated by different methods.

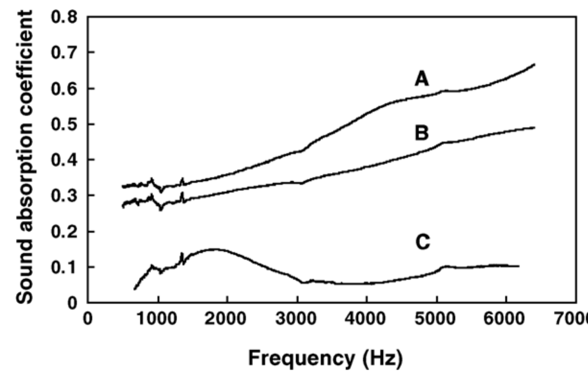

Fig. 4. Sound absorption as a function of frequency for the porous ceramics fabricated by the new method (A) and the conventional method (B), and the dense ceramic tile bought from the market (C).

The broad peaks for this sample indicate that the large pore segments are followed by the smaller ones.

The above results display that porous ceramic sample with a lower density, higher porosity and broad pore size distribution can be fabricated by using the continuous process. We think that the different foaming methods are responsible for the different pore structure of the samples. In the conventional process, the bubbles are introduced into slurry containing only a small amount of surfactant by vigorous stirring under the N_2 atmosphere. Surfactant molecules migrate to the bubbles surface and stabilize the bubbles by decreasing the local surface tension. The migrating process takes considerable time such that bubbles formed at the initial process may collapse before the contact with surfactant. However, in the new process, before mixing with slurry N_2 bubbles are stabilized by surfactant. So, a significant volume of gaseous phase is combined into the slurry and the foamed slurry is more stable. The stabilized bubbles have a much longer time to undergo slurry mixing process and thus have a high opportunity to coalesce to form large bubbles, resulting in a higher porosity and broad pore size distribution of produced sample. These results reveal the new method as a promising technique for the continuous fabrication of porous ceramics. Our former investigation had shown that the porous ceramics fabricated by gelcasting using waste resources have potential for use as outside construction ceramic tile.[9,10] Here, we further study the sound absorption and heat insulation properties of the porous ceramics fabricated by the new method and compare with that prepared using the conventional method.

3.2. Sound absorption property

Noise has attracted much attention because of its harmful effects on the life of human being.[18–20] Sound absorption is an important property of porous ceramics which are used as outside construction materials. The sound absorption characteristics of the two porous ceramics fabricated by the two different methods are shown in Fig. 4. For comparison, a dense ceramic tile bought from the market is tested using the same experimental conditions. The sound absorption coefficient (α) is below 0.2 for the dense ceramic tile, indicating a poor sound absorption performance. On the contrary, the two porous ceramics display obvious high α value. It can be seen that in the sound frequency range studied, α value of the porous ceramic fabricated by our new method is higher than that of the sample fabricated by the conventional method. This illustrates an increase in sound absorption for the former sample. It is accepted that there are mainly two features that are responsible for the absorption of sound. The first is the loss of sound energy due to flexural vibrations in the specimen. The second is the porosity effect, where energy is dissipated by the multiple reflections of sound waves within the voids in the structure. Accordingly, the sound absorption for the porous materials is mainly due to the dissipation of the sound energy within the pores. The porosity of porous materials as well as other material parameters (grain size, flow resistivity, etc.) had been reported to play an important role in the sound absorption performance.[18,20] It can be seen from Table 2 that the porous ceramic fabricated by our new method shows higher open and total porosities, which results in the expected increase of sound absorption coefficient.

3.3. Thermal conductivity

Table 2 shows the thermal conductivity of the two porous ceramics fabricated by the two different methods. The porous ceramic fabricated by our new method represents lower thermal conductivity than that of the sample fabricated by the conventional method, demonstrating a great thermal insulation property for the former sample. As noted previously, the former sample displays higher open and total porosities. According to Sepulveda et al., the higher porosity could enhance the point-defect scattering, which may be a result of the increase in the solid-pore areas and the decrease in the minimum solid areas, and the scattering by Umklapp processes.[21] The other microstructural features also are of great importance. By comparing the thermal conductivity of two kind porous ceramics prepared by different techniques (i.e. gelcasting technique, and dry-pressing and sintering technique), Sepulveda et al. thought that large pores might result in less effective dissipation of heat transfer and a larger mean free-path for phonons to propagate.[21] Table 2 and Fig. 3 show that the porous ceramic fabricated by our new method has a larger mean pore size and a broad pore size distribution than that fabricated by the conventional method. However, the difference of the mean pore size between the two samples fabricated by the same gelcasting technique is not as large as that between the two samples, studied by Sepulveda et al., which were prepared by the different techniques with pore size range of 50–300 μm and 0.05–0.3 μm, respectively. Here, two different trends of thermal conductivity are mentioned, which are associated with the effect of porosity and pore size, respectively. Our results demonstrate that the increase in porosity prevails, leading to low thermal conductivity for the sample fabricated by the new method.

4. Conclusion

Porous ceramics can be fabricated by gelcasting using a continuous process. The mixing of slurry and N_2 bubbles, formed from a separated canister containing a surfactant prior to foaming of slurry, takes place in a spiral mixer. The microstructure parameters, sound absorption and thermal conduction properties of the porous ceramic using this new method are compared with that of sample fabricated using the conventional method. The continuous process gives porous ceramic with lower density and higher open and total porosities, which are thought to result in great sound absorption and thermal insulation properties.

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