A particle-stabilized diatomite foam with a bimodal pore structure

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Diatomite wet foams were stabilized by diatomite particles that were rendered partially hydrophobic by hexylamine, dried, and then sintered. The particle-stabilized diatomite foam contained primary pores with a size of 50 to 200 μm, formed by particles irreversibly adsorbed at liquid–gas interfaces, and secondary pores with a size of about 3 μm, induced by both its irregular particle shapes and inherent pores. In this study, we described a method of preparing diatomite foam with a bimodal pore structure and investigated pore characteristics of the diatomite foam by scanning electron micrographs, mercury porosimetry, and capillary flow porosimetry.

Key-words : Foams, Permeability

1. Introduction

Diatomite is a sedimentary rock resulting from the siliceous fossilized skeleton of diatoms, which are composed of rigid cell walls called frustules.¹ In recent years, there has been increasing interest in diatomite. This low-cost material offers attractive mechanical resistance and can be used as a filter,²,³ filler, or a mild abrasive material due to its highly porous structure. In addition, the frustules of diatoms have nanometer-scale details, and the presence of almost 100,000 species with unique frustule morphologies suggests the possibility of nuanced structural and optical functions well beyond the current ranges used in advanced materials.⁴ Accordingly, a challenging area among applications of diatomite is how to consolidate them as a bulk structure that retains its unique, inherent pores.

With rapid progress in the area of colloidal chemistry, ceramic foams can now be fabricated by incorporating air into an aqueous suspension containing surfactant molecules and then drying and sintering the resulting sample. Numerous studies on particle-stabilized direct foaming methods have been reported.⁵⁻¹⁴ Although the topic of particle-stabilized foam has been well-documented in the literature, previous works have focused on particle-stabilized foam prepared by spherical or uniform particles. It has not yet been established whether irregular and porous diatomite particles can be foamed by a particle-stabilized method. Moreover, diatomite is a composite of materials including silica, alumina, and other oxides, although silica is the main component. Notably, no group, as far as we know, has studied diatomite foams with a bimodal pore structure. A particle-stabilized diatomite foam would potentially contain primary pores formed by particles irreversibly adsorbed at liquid–gas interfaces as well as secondary pores induced by both its irregular particle shapes and inherent pores. Furthermore, foaming by a particle-stabilized method would provide an easy, inexpensive, and fast approach to fabricate highly porous ceramics with a bimodal pore structure.

The aim of this paper is to clarify whether diatomite with a bimodal pore structure can be foamed by a particle-stabilized method. For comparison with particle-stabilized diatomite foams, a sintered diatomite was also prepared by the conventional dry-pressing method.

2. Material and methods

Diatomite (Celite 281, Celite Korea Co. Ltd., Korea) was used for the preparation of particle-stabilized diatomite wet foams. The composition of the as-received diatomite is shown in Table 1. Distilled water was used as a solvent and the slurry was ball-milled for 24 h with a ball to powder ratio of 2:1. After ball milling, 105 mmol/L of hexylamine [(CH₃(CH₂)₅NH₂, 99% pure, Sigma-Aldrich, U.S.A.) was added. The solid loading of diatomite was 45 wt. %, and the final pH was 11.7. Foaming was carried out by using a direct driven motor at a speed of 1000 rpm. In order to slow down the drying process, the prepared particle-stabilized diatomite wet foams were dried for 24 h in a humidity and temperature controlled chamber at 20°C with humidity of 90%. Because micro-cracks were induced by abrupt water elimination, high humidity should be applied to ensure a low driving force for water vaporization during the drying process. After 24 h, the temperature was increased to 30°C under the same humidity conditions.

After drying the specimens, sintering was carried out at 1000–1200°C for 1 h and at 3°C/min of heating and cooling rate. For comparison, green bodies of the diatomite powder with a polyethylene glycol binder were dry-pressed at 18.7 MPa, and then sintered at 1200°C for 1 h. Bulk densities were calculated by measured dimensions and weights. Pore characteristics of the

Table 1. Specification of as-received diatomite (CELITE 281)

| Type     | Weight percent | Type     | Weight percent |
|----------|----------------|----------|----------------|
| SiO₂     | 89.6           | TiO₂     | 0.2            |
| Al₂O₃    | 4              | CaO      | 0.5            |
| Fe₂O₃    | 1.3            | MgO      | 0.6            |
| P₂O₅     | 0.2            | Na₂O + K₂O | 3.3         |

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diatomite foam were investigated by scanning electron micrograph (JSM-5800, JEOL, Japan), mercury porosimetry (Autopore IV 9510, Micromeritics, U.S.A.), and capillary flow porosimetry (CFP-1200-AEL, Porous Materials Inc., U.S.A.).

3. Results and discussion

In this study, we obtained particle-stabilized diatomite foams with a bimodal pore structure by ball-milling diatomite particles for 24 h, and the pore characteristics of those foams were investigated. We could not obtain a stable foam using as-received diatomite or diatomite particles ball-milled for 4 h. Issues regarding the particle characteristics of diatomite are discussed below. The condition for the largest possible size of solid particles that can be utilized to stabilize liquid foams is written as follows:

\[
R_s < \frac{2\sigma}{\left(P_0 + \frac{2\sigma}{R_{\min}} + \rho_f g H\right)}
\]

(1)

where \(\sigma\) is the surface tension of the liquid (J/m\(^2\)), \(P_0\) is the outside pressure of the gas, \(R_{\min}\) is the minimum radius of curvature of the cell wall, \(\rho_f\) is the density of the liquid, \(g\) is the gravitational acceleration constant, \(H\) is the total height of the foam, and \(R_s\) is the size of solid particles. As calculated from Eq. (1), \(R_s\) should then be below 3 \(\mu\)m.\(^{15}\) However, when we reduced the size of diatomite particle below 3 \(\mu\)m by mechanical milling, the unique shape of the fossilized skeleton of diatoms collapsed. We hence hypothesized that the diatomite particles could be foamed by a particle-stabilized method even when the particle size was above 3 \(\mu\)m. As the particle shape of diatomite is not spherical, but rather irregular and porous, the gas bubbles in the slurry might be covered with several layers of diatomite particles as opposed to a single layer of spherical particles. This assumption might be explained as follows: The particle-stabilized direct foaming method is intrinsically based on the idea that particles can be used to adsorb irreversibly on the surface of gas bubbles to stabilize wet foams. Upon adsorption, particles lower the overall free energy of the system by replacing part of the high-energetic gas-liquid interfacial area with a less energetic interface. Therefore, if the particles are uniform and spherical, the surfaces of the gas bubbles will be covered with several layers of particles. Even though there are many inter-particle voids induced by irregular particles, the state where the surfaces of gas bubbles are covered with as many particles as possible is energetically favorable. If the diatomite particle settles too rapidly and does not disperse properly in the water-based solution, it will be difficult to maintain a particle-stabilized foam. Therefore, the effect of sedimentation in accordance with varying particle size should be considered. If the particles descend in the viscous fluid by their own weight due to gravity, then the settling velocity is reached when the frictional force combined with the buoyant force exactly balance the gravitational force. The resulting settling velocity is given by Stoke’s law.

\[
V_s = \frac{2(\rho_f - \rho_p)gR^2}{\eta}\]

(2)

where \(V_s\) is the particles’ settling velocity, \(g\) is the gravitational acceleration, \(\rho_f\) is the mass density of the particles, and \(\rho_p\) is the mass density of the fluid. \(\eta\) is the dynamic viscosity of the fluid, \(R\) is the radius of the spherical particle. Therefore, in this study, we controlled the particle characteristics by mechanical ball-milling. The particle size distributions of as-received diatomite, diatomite ball-milled for 4h, diatomite ball-milled for 24h, and diatomite ball-milled for 168h are shown in Fig. 1(a). The average particle sizes of diatomite as-received, ball-milled for 4h, ball-milled for 24h, and ball-milled for 168h were 20.34, 24.31, 31.73, and 38.49 \(\mu\)m respectively. As the settling velocity is proportional to the square of the radius of a particle, the settling velocity of diatomite ball-milled for 24h was about 1/9th that of the as-received specimen. Therefore, considering background addressed above, one of the important factors with respect to the stability of the diatomite foams is particle size. Figures 1(b) and 1(c) show that the diatomite foam maintained both the unique shapes and inherent pores of the fossilized skeleton of diatoms in the case of the as-received and the 24h ball-milled specimens, respectively, unlike the 168h ball-milled specimens, as shown in Fig. 1(d).

Also we varied the amount of hexylamine from 65 to 125 mmol/L, only the diatomite specimen with 105 mmol/L of hexylamine addition maintained a stable foam shape after drying. And it can be well explained by the effect of amphiphile concentration on the particles in slurry.\(^{3,9,13,14}\) The specimen that
was conventionally dry-pressed and sintered at 1200°C for 1 h specimen is shown in Fig. 1(e).

The diatomite foams had rigid strut walls after the sintering process, as shown in Figs. 2(a)–2(c). These sintered foams showed similar microstructures when sintered at up to 1200°C, with cell sizes ranging from 50 to 200 μm, and with unique multiple layered strut walls, as expected. The densities of diatomite foams sintered at from 1000, 1100, 1200, and 1300°C, were 0.32, 0.37, 0.42, and 0.51 g/cm³, respectively, which are proportional to the sintering temperature because of the densification of diatomite grains during the sintering process. In Fig. 2(d), a clear coalescence of porous diatom frustules and grains is seen in samples sintered at 1300°C, and therefore the average pore size decreased.

It is suggested that the collapse of the inherent pore structure of diatomite at 1300°C was induced by impurities in diatomite such as Na₂O, K₂O, Al₂O₃, CaO and MgO. These impurities favor low temperature eutectics and thus the formation of a melt phase in the silica rich grains.¹⁶ As presented in Fig. 3(a), the average pore size of sintered diatomite foam increased as the sintering temperature was increased up to 1200°C. These trends are in good agreement with the experimental results covering different porous ceramics such as diatomite,¹⁵ silicon carbide,¹⁷¹⁸ alumina,¹⁹ corundum-mullite²⁰ and zirconia²¹ at different temperature ranges. Although this is generally explained by pore coarsening,¹⁵ or densification,¹⁹ and processing routes to produce porous ceramic foams have also been extensively documented in the literature, the relation between average pore size and sintering temperature has not yet been established. In this paper, we did not focus on the sintering behavior of the particle-stabilized diatomite foam, but rather the pore characteristics and permeation properties of the particle-stabilized diatomite foam. Therefore, this is an important issue for future research. As we observed that the partial melting of the pore structure at 1300°C, Fig. 3(b) shows that the pore size of the foam was not increased any further. In addition, the conventionally dry-pressed and sintered specimen had pores corresponding with the secondary pores of the particle-stabilized diatomite foams. The air permeation properties of diatomite foam were proportional to sintering temperature only up to 1200°C, as can see in Fig. 3(c). Both the diatomite foam where partial melting occurred at 1300°C and dry-pressed and sintered diatomite showed relatively low air permeation properties, as presented in Fig. 3(d). It is thus noteworthy that the air permeation properties were enhanced by the primary pores of the particle-stabilized diatomite foam. These findings show the feasibility of using a particle-stabilized diatomite foam in the filtration area.

4. Conclusions

In summary, we synthesized diatomite foams that have primary pores with a size of 50 to 200 μm, formed by particles irreversibly adsorbed at liquid–gas interfaces, and secondary pores with a size of about 2 to 5 μm. We suggested that irregular and porous diatomite particles could be foamed on condition that the particle size was below than 10 μm. After being sintered at up to 1200°C for 1 h, the diatomite foam maintained both the unique shape and the inherent pores of the fossilized skeleton of diatoms. The air permeation properties of the diatomite foam were proportional to the sintering temperature up to 1200°C, which was enhanced by primary pores, and could increase filtration potential.

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