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Control of pore size in ceramic foams: Influence of surfactant concentration

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ABSTRACT

The role of sodium lauryl sulfate (SLS) on pore size of ceramic foams has been investigated using silica foams with 65–70% porosity prepared by a mechanical foaming and gelcasting method. Experiments were carried out to determine bubble size and stability of three-phase foams as well as the pore size of ceramic foams under a range of SLS concentration. Results suggested that pore size of ceramic foams is successfully controlled by changing the SLS concentration of three-phase foam slurries. The controllable range of pore size in this study was roughly 70–150 μm, which corresponded to the SLS concentration range between 7×10^{-3} and 7×10^{-2} M. Furthermore, it was found that the SLS concentration significantly influenced on the foam stability during post-foaming processes as well as the initial bubble size.

1. Introduction

Ceramic foams are known to have high permeability, high specific surface area, good insulating characteristics, high refractoriness, chemical resistance, and long life in severe environments due to their high porosity, well-developed surface pores, and three-dimensional network pore structure [1–9]. Those characteristics enable ceramic foams to be widely used in industrial fields as filters for contaminated hot gas purification [3,4,10] or solid/liquid separation process [4], catalyst carriers [11,12], refractories [4,13], thermal insulators [4,13], and biomedical substitutes with skeletal and dental functions [2,14].

Two representative methods, a polymeric sponge method [4,15,16] and a foaming method [4,6,17], have been commonly utilized to prepare ceramic foams. Among these, the foaming method has an advantage in that it can conveniently control the pore structure of ceramic foams by artificially controlling the foam volume expansion ratio ($\mathrm{ER_{FV}}$), which is defined as the ratio of volume of the foamed slurry to that of original. Therefore, developing highly stabilized three-phase (solid–liquid–gas) foams is the first and most critical step to prepare suitable ceramic foams [17,18]. In many cases, such a foaming process generates a high density of bubbles and disperses them in the foam slurry. The bubbles are finally converted into pores between solid particles in the ceramic foam through shaping and heating processes [3,8,9]. Therefore, pore-related parameters (porosity, pore size, and pore morphology) can significantly affect the global characteristics of the ceramic foams, such as the specific surface area, water absorption, surface roughness, and permeability. Pore size in particular is one of the most important properties in determining the practical applications of ceramic foam [18]. Consequently, the variation and control of bubble size and the corresponding pore size in foam slurry deserve academic investigation; however, some researchers have only focused on bubble size in three-phase foam slurries, pore size in ceramic foams, and the interrelation between them. Park et al. [3] reported that the type of surfactant is the more important factor than surfactant concentration in controlling bubble sizes and the corresponding pore sizes in cordierite ceramic foams. Mao et al. [19], on the other hand, observed that the maximum $\mathrm{ER_{FV}}$ of alumina foam slurries can be significantly affected by surfactant concentration at a uniform condition, indicating that the surfactant concentration can play an important role on the stability and bubble sizes of the three-phase foams. Therefore, the objective of our study is to control the pore size in silica ceramic foams, which is achieved through varying the bubble size by changing surfactant concentration.

2. Experimental procedure

The following experimental materials were used to prepare well-dispersed slurry: sodium lauryl sulfate (SLS, Samchun Pure Chemical Co., Korea) as a foaming agent, about 1×10^{-3} M sodium hexametaphosphate (SHP, Samchun Pure Chemical Co., Korea) as a dispersant, and distilled water were mixed with silica powders of less than 3 μm in size. The solid loading of the prepared slurries was 40 vol.% for all experiments. Temperature and pH of aqueous solution were fixed to 25 °C and 7.0 ± 0.2, respectively. The well-dispersed slurry was stirred at 300 rpm for 50 min to

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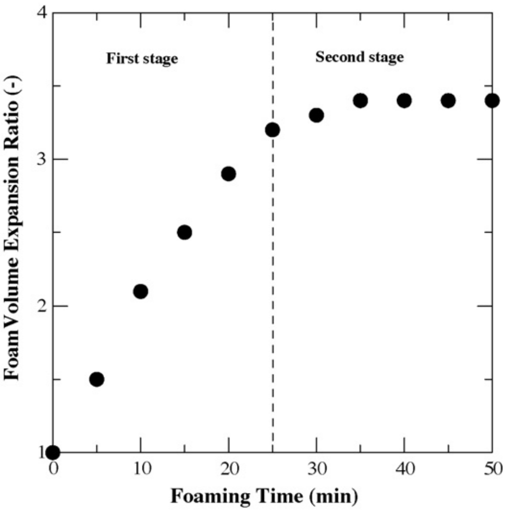

Fig. 1. Representative foam volume expansion ratio (ER_{FV}) and the corresponding foaming stages during agitation. SLS concentration was 1×10^{-2} M.

generate foam, using a stirrer equipped with rectangular typed blades of two steps, with 1.4 mm-thick blades at a 5-mm interval and twisted for deriving a downward airflow direction during rotation. The rapid agitation with blade rotation was effective not only for air injection into the slurry to generate foams, but also for dissolution of SLS and SHP. The foaming reactor was a 1000-cm^3 commercial plastic beaker. The bubbles in the completely dispersed foam slurry were immediately examined using an image analysis system (Image-Pro Plus Ver. 2.0, Media Cybernetics, USA) [20].

After the foaming process, the gelation agents, 3.5 wt.% polyethyleneimine (PEI, Lupasol-HF, BASF Co. Ltd., Germany) and 1.2 wt.% epoxy resin (Denacol-EX614B, Nagase Chemicals Co. Ltd., Japan) were then carefully added to the foam slurry with constant mixing at 300 rpm for 1 min. The green bodies were dried in air at 70 °C for 2 h. Pyrolysis of the dried green bodies was carried out at 600 °C in air for 1 h, and they were sintered with an electric furnace (51314, General Signal Co., UK) at 1200 °C for 5 h using heating rates of 100 °C h^{-1} up to 600 °C and then 200 °C h^{-1} up to the final temperature in air. Total porosity of the ceramic foams was measured by gravimetric method and ranged between 65 and 70%. The microstructures of the ceramic foams were observed by scanning electron microscopy (SEM, JSM-6300, JEOL Co., Japan).

As preliminary experiments the adsorption capacity on silica particles and the critical micelle concentration (CMC) of SLS were determined. First, to estimate the adsorption capacity of SLS on silica particles, SLS concentration was measured in solution using a spectrophotometer (DR/2010, Hach Co., USA). The adsorption reactions were carried out in test tubes at 25,000 rpm of centrifugal separation for 30 min. The coloring agent was sodium chloride, and the wavelength at the measuring point was 605 nm. As a result, the equilibrium SLS concentration at the maximum adsorbed amount was about 4×10^{-3} M, which was equivalent to about 0.6 mg SLS/g silica in adsorbed amount. Second, the CMC of SLS in water was determined through dilating the SLS aqueous solution with nitrogen gas-injection (30 cm^3 min^{-1}) in a glass cylinder of 40 mm inner diameter. The CMC was determined to be approximately 7×10^{-3} M.

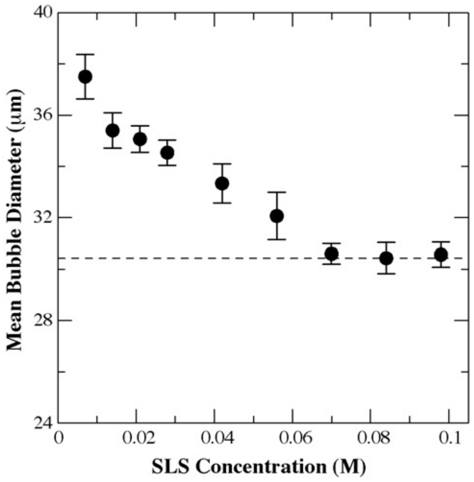

Fig. 2. Mean bubble diameter in the foamed slurry according to SLS concentration ($ER_{FV} = 2$). Error bars indicate one standard deviation.

3. Results and discussion

The volume increase of a foamed slurry as a function of foaming (agitation) time is shown in Fig. 1. The experiment was conducted with 1×10^{-2} M of SLS. At the first stage, the foam volume linearly increased and, at the later stage, remained constant as the agitation elapsed. The reason for such stagnation is due to the depletion of SLS to generate new bubble interfaces, the difficulty in air injection into the foam slurry with rising foam, and the liquid drainage and the film thinning effects causing bubble breakage [21,22]. The result suggested that too significant progressiveness in foaming dilation can prevent the stability of the foam slurry and the development of resultant pore structure of ceramic foams. Therefore, we determined that the acceptable increase of foam volume is up to two times the initial slurry volume (i.e., $ER_{FV} = 2$). Since it was impossible to achieve $ER_{FV} = 2$ at less than CMC ($\leq 7 \times 10^{-3}$ M), we considered the variation of bubble size only in the case of greater than CMC ($\geq 7 \times 10^{-3}$ M). Furthermore, as SLS concentration increased, the foaming time required for $ER_{FV} = 2$ decreased over a low concentration range (7×10^{-3} to 7×10^{-2} M), because lower surface energy was required to produce new bubbles; however, the foaming time became relatively invariable at a higher concentration range than 7×10^{-2} M. This trend was consistent with constantly decreasing tendency of bubble size with increasing SLS concentration up to 7×10^{-2} M as shown in Fig. 2. It was observed that the bubble size initially decreased up to 7×10^{-2} M of SLS addition, and finally reached plateau. This phenomenon can be explained by the following Laplace equation [21,23], which describes the pressure difference between the inside and outside of a bubble (ΔP):

$$\Delta P = \gamma_{\text{air/slurry}} \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \tag{1}$$

where R_1 and R_2 are the two principal radii of curvatures of a bubble, and $\gamma_{\text{air/slurry}}$ is defined to be the apparent surface energy between air in the bubble and the silica/water visco-elastic slurry. Unlike the case of two-phase foam, SLS molecules reduce the surface energy $\gamma_{\text{air/slurry}}$ through the adsorption on the silica/water interfaces in three-phase foam in this study. Consequently, bubbles are surrounded by SLS-coated silica particles as well as by water interfaces, as presented in Fig. 3. A bubble interface with the sur-

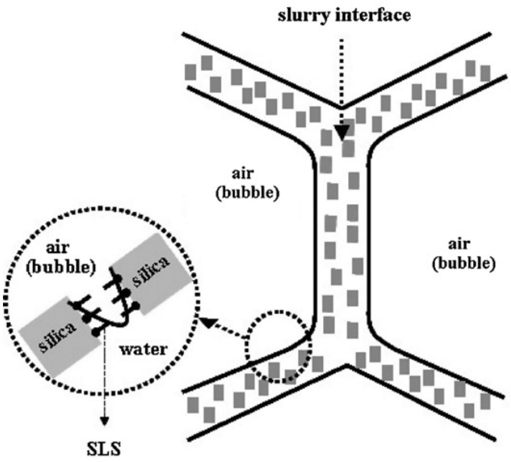

Fig. 3. Schematic illustration for bubbles surrounded by water and SLS-coated silica particles.