

Influence of amphiphile on foam stability of Al₂O₃-SiO₂ colloidal suspension to porous ceramics

Naboneeta Sarkar^a, Jung Gyu Park^a, Dong Nam Seo^a, Sangram Mazumder^a, Ashish Pokhrel^b, Christos G. Aneziris^b and Ik Jin Kim^{a,*}

^aInstitute of Processing and Application of Inorganic Materials, (PAIM), Hanseo University # 360, Seosan-si, Chungnam, 356-706, Korea

^bInstitute of Ceramics, Glass and Construction Materials, Freiberg University, Agricolastrasse 17, 09599 Freiberg, Germany

The stabilization of wet foam is very important to avoid the instability caused by the large interfacial area at gas-liquid interface of colloid suspension. Propionic acid, a short chain carboxylic acid is used as foam stabilizer, which acts by modifying the particle surface and increases the wet foam stability. The characterization of Al₂O₃-SiO₂ foams, namely Laplace pressure, foam stability, air content and bubble size are explored by changing the concentration of the amphiphile. Macroporous Al₂O₃-SiO₂ ceramics with open or closed cells, average pore size of less than 100 μm and porosities within 43 and 51% was prepared by direct foaming process. The sample sintered at 1300 °C for 1 hour showed an adsorption free energy of 0.9×10^7 to 2.0×10^8 kTs and a Laplace pressure of 0.63 to 0.85 mPa, highlighting good wet foam stability of approximately 80-90%.

Key words: Porous ceramics, Direct foaming, Wet foam stability, Carboxylic acid, Laplace pressure, Adsorption free energy.

Introduction

Wet foams are used as intermediate products to produce solid porous ceramics with a range of applications in catalysis, adsorption and separation, filtration of molten metal or hot gases, refractory insulation of furnaces, as well as hard tissue repair and engineering [1]. On the other hand, the liquid foams are thermodynamically unstable because of their large interfacial area, resulting in bubble coarsening as a result of disproportionation, drainage and coalescence [2-4]. Moreover, gas diffusion occurs from smaller to larger bubbles, which leads to broadening of the bubble size distribution, due to different pressures of bubbles with different sizes [5].

This study evaluated a novel and versatile method, the in-situ hydrophobization of initially hydrophilic particles. This process enables the preparation of a high volume of wet foams by stabilizing the particles with short chain amphiphilic molecule containing less than 6 carbon atoms in the hydrophobic tail, as shown in Fig. 1. The anchoring group of the molecule attaches to the particle surface and promotes the surface hydrophobization of colloidal particles [6-9]. The contact angle and surface tension of the colloidal suspension were evaluated to determine if the desired in-situ hydrophobization had taken place. These partially hydrophobized particles are adsorbed to the air-water interface during the process

of mechanical frothing, which resulted in high volume stable wet foams [10].

The microstructural features of wet foam, such as the mean bubble size, Laplace pressure and the air content have a marked influence on the final mechanical and physical properties of porous solid structures [11-13]. These parameters are evaluated by modifying the concentration of the amphiphile to produce stable wet foam. Finally, the processing of porous ceramics, which includes drying and sintering, was developed and final microstructure and its porosity are described.

Experimental Procedure

Materials

The inorganic oxide particles used in the experiments were (i) α-Al₂O₃ powder (KC, South Korea) with a mean particle diameter (d₅₀) of 4 μm and density of 3.95 g/cm³; (ii) SiO₂ powder (Junsei Chemicals Co. Ltd, Japan) with a mean particle diameter (d₅₀) of 3.5 μm and density of 2.65 g/cm³. The short chain amphiphilic molecule used for particle modification was propionic acid (Fluka Analytical, Germany). Double deionized water was used for suspension preparation and volume adjustment. 10 M Hydrochloric acid (HCl) (Yakuri Pure Chemicals, Osaka, Japan), and 4 M sodium hydroxide (NaOH) solutions (Yakuri Pure Chemicals, Kyoto, Japan) were used for the pH adjustments.

Preparation of suspensions

An aqueous suspension of α-Al₂O₃ was prepared by adding the powder to deionized water. The de-

*Corresponding author:
Tel : +82-41-660-1441
Fax: +82-41-660-1402
E-mail: ijkim@hanseo.ac.kr

agglomeration of the colloidal particles was performed by ball milling the suspension in polyethylene bottles for 48 hours using zirconia balls (10 mm in diameter) with a ball/powder ratio 2 : 1. After ball-milling, the short chain carboxylic acid of different concentrations (0.05, 0.10, 0.15 and 0.2 mol/L) was added drop wise to the suspension under mechanical stirring. The amphiphiles were added as concentrate, no prior dissolution had been carried out. The pH of the suspension was then adjusted to 4.75 by adding 4 M NaOH and/or 10 N HCl drop wise. The solid content of the final aqueous suspension was set to 30 vol% and achieved by dilution with additional water. Finally, aqueous suspension of unmodified SiO_2 powder, which was also ball milled separately in same condition, was added to the surface modified Al_2O_3 suspension in a mole ratio of 1 : 0.25 Al_2O_3 / SiO_2 .

Contact angle and surface tension

The surface tension and contact angle was assessed using a pendant drop method (KSV Instruments Ltd, Helsinki, Finland). The drop volume was fixed to a constant value within the range of 5-10 ml for the amphiphile-containing suspension.

Foaming, drying and sintering

Foaming was performed by vigorously stirring the suspension using a household mixer (150 watt, Super Mix, France) for 15 minutes as shown in Fig. 1. The mean bubble size of the resulting foam was evaluated by optical microscopy in transmission mode (Somtech Vision, South Korea) connected to a digital camera. The cell size of the wet foam was measured using the linear intercept method with linear intercept software (TU Darmstadt, Germany). For each sample, a minimum of 100 bubbles were evaluated. The wet foams were dried in air at 22-25 °C for 24-48 hours. Sintering of the cylindrical dried foams was performed in a Super Kantal furnace (max 1650 °C) at 1300 °C for 1 hour. The heating and cooling rates were set to 1 and 3 °C/min, respectively.

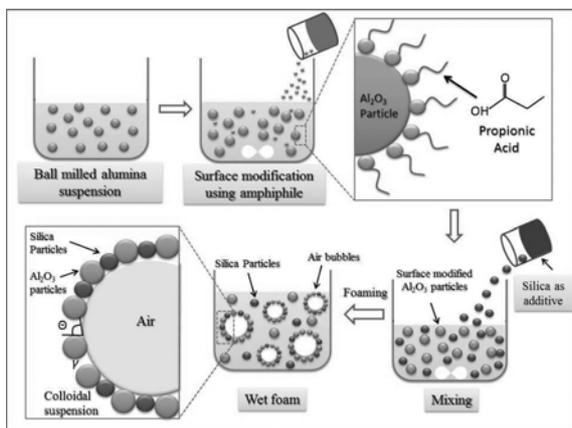


Fig. 1. Schematic diagram of the direct foaming technique.

Results and Discussion

The change in particle hydrophobicity upon the adsorption of short chain carboxylic acid can be monitored by contact angle and surface tension measurements. The attachment of particle at the gas liquid interfaces occurs when particles are not completely wetted in the liquid phase, or in other words, are partially hydrophobic. To achieve this condition, the contact angles were modified by changing the concentration of the amphiphile. As we can see from Fig. 2, 0.05 mol/L concentration of propionic acid was not sufficient to impart particle hydrophobicity which results in unstable foams. From this graph, we can conclude that a contact angle of 65° to 72° produces required particle hydrophobicity, which enables high wet foam stability. The addition of carboxylic acid molecules decreased the surface tension of the suspension, as shown in Fig. 2. The reduction in surface tension results from the adsorption of free amphiphile molecules to the air-water interface. This adsorbed particles replace part of the highly energetic interface area and thus lower the overall free energy. Fig. 2 shows that the suspensions with amphiphile concentrations of 0.15-0.2 mol/L have lower surface tension, resulting in highly stable wet

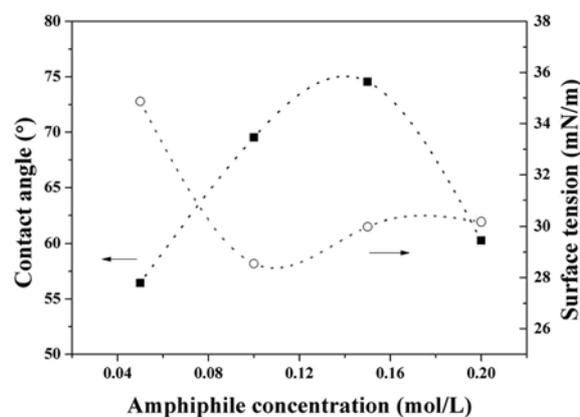


Fig. 2. Contact angle and surface tension of the suspension with respect to different concentration of amphiphile.

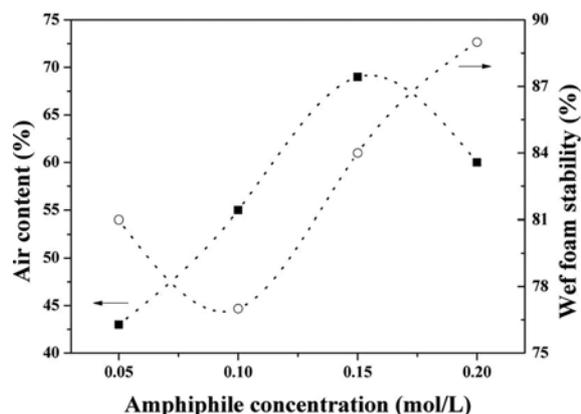


Fig. 3. Air content and wet foam stability of the suspension with respect to different concentration of amphiphile.

foams.

Fig. 3 is a graphical representation between air content and wet foam stability of the suspension with respect to different concentration of amphiphile. To investigate the wet foam stability the wet foam samples were filled into cylindrical molds of constant volume and left for 48 hours. Foam stability was evaluated upon observing the percentage of volume loss of the foam.

$$\text{Wet foam stability} = \frac{V_{\text{Final}}}{V_{\text{Initial}}} \times 100 \quad (1)$$

Where V_{Final} indicates volume of wet foam after 48 hours and V_{Initial} indicates volume of wet foam before 48 hours.

Air content was measured by calculating the percentage of volume increase in the suspension after foaming.

$$\text{Air content} = \frac{(V_{\text{wet foam}} - V_{\text{suspension}}) \times 100}{V_{\text{wet foam}}} \quad (2)$$

Where $V_{\text{wet foam}}$ indicates the wet foam volume after foaming and $V_{\text{suspension}}$ indicates volume of suspension before foaming. The wet foams obtained after mechanical frothing exhibited air contents up to 69% at an amphiphile concentration of 0.15 mol/L. On increasing the concentration of propionic acid from 0.05 mol/L to 0.15 mol/L, the air content of the foam firstly increased from 43% to 69% and then decreased to 60% at higher amphiphile concentration. The increased air contents attribute to the formation and subsequent stabilization of air bubbles due to the attachment of particles to the air-water interface. Whereas, the decrease in air content at high amphiphile concentration of 0.20 mol/L of propionic acid is due to increase of suspension viscosity which resists the air incorporation to the suspension and results in foam with lower air contents.

Fig. 4 shows the change in adsorption free energy corresponding to the different concentration of amphiphile used to stabilize the suspension. The energy of attachment or free energy gained (G) by the

adsorption of a particle of radius (r) at the interface can be calculated using the following equation:

$$\Delta G = \pi r^2 \gamma (1 - \cos \theta)^2 \text{ for } \theta < 90^\circ \quad (3)^{14}$$

Where γ is the surface tension of the suspension and θ is the contact angle. The graph shows a range of high adsorption free energy with different amphiphile concentration. Upon adding 0.05 to 0.20 mol/L concentration of amphiphile, adsorption free energy of about 9.0×10^7 to 2.0×10^8 kT is achieved. This high energy is associated to the adsorption of particles at interfaces which forces the suspension to stabilize and exhibits a high wet foam stability of about 85% to 90%. Whereas foams stabilized with surfactants show adsorption free energy in the order of 10^3 kTs which implies that it takes much less energy to desorb a surfactant molecule from air-water interface than a particle. It results from the irreversible adsorption of particles at the air-water interface which leads to outstanding stability.

The pressure acting between two air bubbles, resulting in Ostwald ripening, which is one of the important phenomena of the wet foam instability, can be measured by a Laplace pressure evaluation. The Laplace pressure (ΔP), implying the difference between the inside and outside pressure of a gas bubble is a major parameter to consider for stabilization mechanism.

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} \text{ (Spherical bubble)} \quad (4)^{15}$$

where γ is the surface tension of the suspension and R_1 , R_2 are the radius of two interfacing bubbles. In our experiment the bubbles are almost spherical and due to the narrow size distribution we used the above equation. Fig. 5 shows the Laplace pressure and wet foam stability with respect to the different concentration of amphiphile. Both the Laplace pressure and wet foam stability increased with increasing amphiphile concentration. Higher Laplace pressure attributed to finer bubbles in

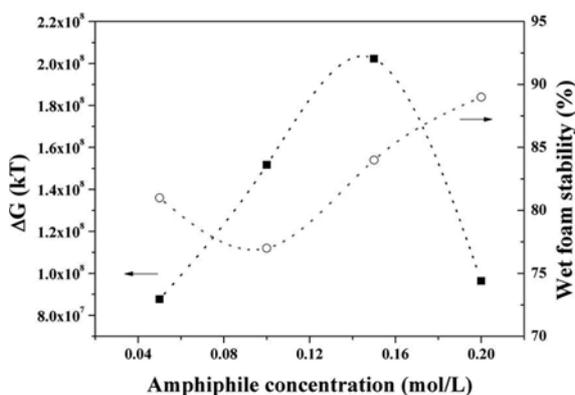


Fig. 4. Free energy and wet foam stability with respect to different concentration of amphiphile.

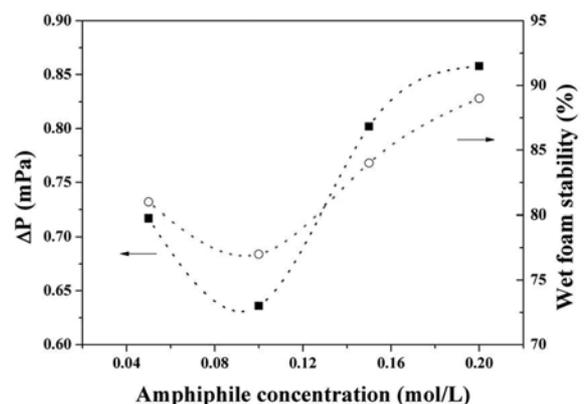


Fig. 5. Laplace pressure and wet foam stability with respect to different concentration of amphiphile.

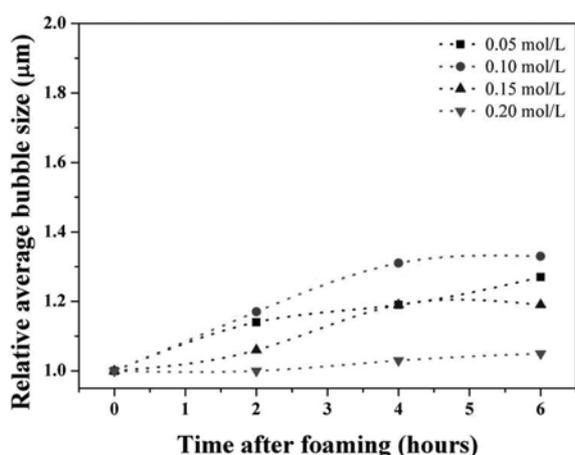


Fig. 6. Relative average bubble size of different concentration of amphiphile with respect to time after foaming.

the system. As we can see, Laplace pressure increased from 0.10 to 0.20 mol/L, where the bubble size decreased from 98 to 73 μm . Foams with lower bubble sizes enable high stability of system. The highest wet foam stability of approximately 80-90% was achieved at an amphiphile concentration of approximately 0.15-0.20 mol/L when the Laplace pressure was between 0.80 to 0.86 mPa.

The relative average bubble size corresponds to the ratio between actual and initial average bubble size. Fig. 6 shows relative average bubble size of different concentration of amphiphile with respect to time after foaming. The foams with high amphiphile concentration showed no significant bubble growth for 6 hours after foaming. On the other hand, remarkable bubble coarsening is observed in foams with lower amphiphile concentration due to the pressure difference between two bubbles of different radius which leads to Ostwald ripening. This thermodynamically-driven spontaneous process occurs because the internal pressure of a particle is indirectly proportional to the radius of that particle. Large particles, with their lower surface to volume ratio, results in a lower energy state (and have a lower surface energy). As the system tries to lower its overall energy, molecules on the surface of a small (energetically unfavourable) particle will tend to detach and diffuse through solution and then attach to the surface of larger particle. Therefore, the number of smaller particles continues to shrink, while larger particles continue to grow [16].

The bubble size and porosity can also be tailored by modifying the amphiphile concentration. Fig. 7 shows the mean bubble size of the wet foam and porosity of the sintered sample as a function of the amphiphile concentration. The concentration of the amphiphile has a marked influence on the bubble size distribution. Despite the wet foams having nearly 70% air contents, their average bubble sizes decreased from 107 to 73 μm

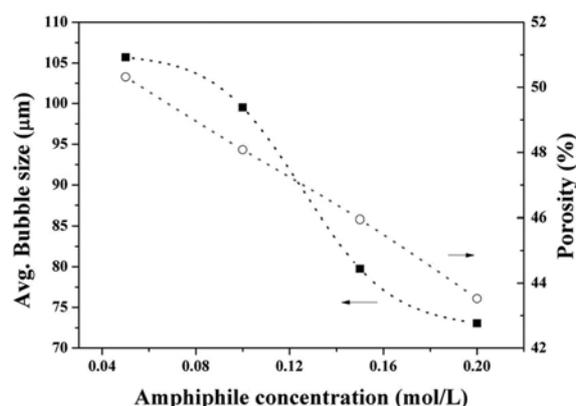


Fig. 7. Average bubble size and porosity with respect to different concentration of amphiphile.

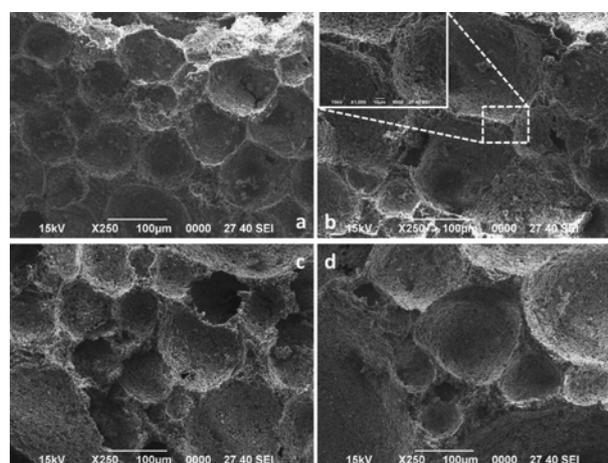


Fig. 8. SEM images of the microstructures and thin films (inner cell) of 30 vol% $\text{Al}_2\text{O}_3\text{-SiO}_2$ porous ceramics sintered at 1300 $^{\circ}\text{C}$ with (a) 0.05 (b) 0.10 (c) 0.15 and (d) 0.20 mol/L of amphiphile.

as propionic acid concentration increased from 0.05 to 0.20 mol/L. The optimal amphiphile concentration (0.15-0.20 mol/L) produced foams with a narrow bubble size distribution and good wet foam stability. The porosity also decreased from 51 to 43% with decreasing bubble size from 107 μm to 73 μm .

Fig. 8 presents the microstructures of the $\text{Al}_2\text{O}_3\text{-SiO}_2$ porous ceramics sintered at 1300 $^{\circ}\text{C}$ with different amphiphile concentrations, where mainly closed pores can be seen. In addition, a well-developed and uniform pore size distribution can be observed with an average cell size of less than 100 μm . The smaller cell sizes resulted from the higher wet foam stability which hinders drainage and bubble coarsening. Fig. 8(b) shows intercellular film with a range of thicknesses from 3 to 7 μm (picture was shown in the inset), which plays a vital role to produce stable sintered porous ceramics. Comparative porosity analysis data (measured by Micromeritics) of the samples showed porosity up to 51%.

Conclusions

Inorganic oxide particles, such as Al_2O_3 and SiO_2 can be hydrophobized partially using short chain carboxylic acid to produce wet foams with high air contents of about 55% to 68% and remarkable wet foam stability. Hydrophobization of the Al_2O_3 - SiO_2 surface was achieved through the adsorption of propionic acid, exhibiting a functional hydroxyl group that efficiently anchors to the particle surface and a short hydrophobic tail that remains in contact with the aqueous phase. The surface tension and contact angle measurements showed that the particles need to be sufficiently hydrophobized to adsorb to the air water interface. The high stability of wet foams means that they can be shaped, dried in air and sintered. Overall, a versatile process for stabilizing inorganic oxide particles in the processing of porous ceramics was performed, and wet foams with remarkable stability are produced.

Acknowledgments

This research was financially supported by Hanseo University and also the co-operation between the Korean and the German group was supported by the Collaborative Research Centre 920 of the German Scientific Foundation (DFG).

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