

Controlling the Porosity of Particle Stabilized Al₂O₃ Based Ceramics

Ashish Pokhrel, Jung Gyu Park, Gae Hyong Jho, Jin Young Kim, and Ik Jin Kim[†]

*Institute of Processing and Application of Inorganic Materials (PAIM)
Department of Advanced Materials Science and Engineering, Hanseo University, Seosan 356-706, Korea*

(Received September 1, 2011; Revised September 8, 2011; Accepted September 8, 2011)

ABSTRACT

The microstructure of particle stabilized wet foams can be tailored by using parameters including the amphiphile concentration, contact angle, and surface tension. The influence of these parameters on the porosity is satisfactorily described in terms of a combined influence of the contact angle and surface tension of the initial suspensions that are directly affected by the amphiphile concentration. The resulting macroporous structures exhibited a total porosity of 82%. The foam cells were predominantly closed due to the air bubbles of the original wet foams being completely covered.

Key words: Contact angle, Amphiphile concentration, Surface tension, Wet foams, Porosity

Introduction

The concentration of amphiphilic molecules in the initial suspension and the lengths of their hydrophobic tails can be used to tailor the alumina particle surface hydrophobicity in water. Inducing suitable hydrophobicity allows homogeneous foaming throughout the suspension upon mechanical frothing. The stabilities of the foams obtained in this study resulted from the different stabilization mechanisms of the air-water interface from those applied in the conventional shaving foam. In ceramic foams, particles are used as stabilizers; however in shaving foam, conventional amphiphilic surfactants are used to stabilize the air-water interface. The irreversible adsorption of particles into the interface results in a percolating interfacial armor that mechanically impedes bubble growth, shrinkage, and coalescence.^{1,2)} Adsorptions at fluid interfaces occur when the particles are not completely wetted, thus exhibiting a final equilibrium contact angle at the triple phase boundary. The equilibrium contact angle (θ) is determined using a balance between the interfacial tensions involved. Similar to the hydrophile lipophile balance (HLB) used for surfactant stabilized systems; the contact angle determines the type of mixtures to be formed. Oil in water emulsions and foams is obtained for contact angles lower than 90°, whereas water in oil emulsions and mists (aerosols) are produced for contact angles varying from 90° to 180°. ^{3,4)} Likewise, the air content bubble size, and bubble size distribution of wet foams used to produce porous materials also have a remarkable influence on the final mechanical and physical properties of porous solid structures. ^{5,6)} Particles

with a high aspect ratio and/or that exhibit hysteresis of the contact angle are particularly efficient in preventing bubble/droplet coalescence. The stability toward Ostwald ripening, however, has been explained by the mechanical resistance of the outer particle layer to the shrinkage and/or expansion of droplets and gas bubbles. The high stability rendered by the particles adsorbed on the surface of the droplets and bubbles is a key feature for the preparation of tailored materials from foams and emulsions. ^{7,8)}

The degree of particle hydrophobization achieved through the surface adsorption of amphiphiles has been investigated with assistance of surface tension measurements. A decrease in the surface tension upon an increase in the initial amphiphile concentration in the solution has been observed for all evaluated suspensions. However, above a critical amphiphile concentration, a relatively strong decrease in the surface tension has been observed. ^{8,9)} Above this critical amphiphile concentration, the particles were sufficiently hydrophobic to attach to the air-water interface, leading to a more pronounced decrease in the surface tension than that expected from the free amphiphiles alone. This significant reduction in surface tension upon particle adsorption was caused by a decrease of the total area of the highly energetic air-water interface. ¹⁰⁾ In this study, the final tailored microstructures and stability of the wet foams were characterized through measurements of the contact angle, surface tension, and porosity. Unmodified silica particles were added and were expected to form networks throughout the foam lamellae, in order to aid the prevention of bubble coarsening. Propyl gallate was used as the amphiphile that induced hydrophobicity into the alumina particle surfaces.

2. Materials and Methods

2.1. Materials

High-purity alumina was obtained from Showa Chemical,

[†]Corresponding author: Ik Jin Kim
E-mail: ijkim@hanseo.ac.kr
Tel: +82-41-660-1441 Fax: +82-41-660-1402

Tokyo, Japan, and silica was obtained from Junsei Chemical, Japan. Deionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China) were also used.

2.2. Suspension Preparation

The suspensions were prepared using propyl gallate as an amphiphile through the stepwise addition of alumina powder to an aqueous mixture of 0.01 M NaOH and 0.1 M propyl gallate. The solid loadings and pH of the suspensions were initially fixed at 50 vol% and 9.9, respectively. Homogenization and de-agglomeration were performed via ball milling for at least 24 hours using polyethylene milling pots and alumina balls (10 mm in diameter - 2 : 1 ratio of balls to powder). The propyl gallate was adjusted to the required concentration in the final suspension (1-2 wt% to Al₂O₃). This was dissolved in NaOH (pH > 10) and added dropwise to the ball milled suspension under slight stirring in order to avoid local particle agglomeration. Finally, the pH was set at 9.9 and water was added until the solid contents were 30 vol%. In other experiments, suspensions under various pHs were also tested.

The SiO₂ suspensions were prepared through the addition of dry silica powder to water to achieve solid loadings of 45 vol%. The silica was unmodified and no further pH modification was required. The suspensions were then de-agglomerated and homogenized via alumina ball milling. Through stirring, the silica was added dropwise to the alumina suspensions containing propyl gallate. The pH was set as 9.9; it was varied in other tests. The total solid content of the mixture was fixed at 30 vol%. Various blends of modified and unmodified particles were prepared and tested with a total solid content of 30 vol% under varying pH conditions.

2.3. Contact Angle and Surface Tension

The contact angles and surface tensions of the suspensions were measured using the pendant drop method (KSV Instruments Ltd, Helsinki, Finland). Alumina suspensions were prepared through the dropwise addition of propyl gallate to generate solid loadings of 30 vol% alumina. The drop volume was varied between 5 and 10 μ l depending on the suspension contact angle and surface tension.

2.4. Foaming, Drying, and Sintering

The foaming of 150 ml suspensions was performed using a household mixer (150 watt, Super Mix, France) at full power for 3 to 5 minutes. The bubble size distributions of the foam were evaluated via optical microscopy in the transmission mode (Somtech Vision, South Korea) with a connected digital camera. The bubbles sizes were measured using linear intercepts. The average sizes were determined from analyses of particular areas. Wet samples were shaped into cylinders by hand and subsequently dried in air at 20-25°C for 24-48 h. The dried foams were sintered in an electric muffle furnace at 1200°C for 2 h. The heating rate was 1°C/min and the cooling rate was 3°C/min.

3. Results and Discussion

3.1. Initial Amphiphile Concentration

The effects of the amphiphile strength on the contact angle and wet foam stability were assessed and are shown below in Fig. 1. The amphiphile concentration of the initial suspension directly affects the colloidal particle hydrophobicity; varying the particle concentration with a constant amphiphile addition also affects the particle hydrophobicity. Increasing the initial amphiphile concentration increases the adsorption into the particles, resulting in enhanced surface hydrophobicity. Above a critical concentration of adsorbed amphiphiles, the particles become sufficiently hydrophobic to adsorb into the air-water interfaces, stabilizing the freshly introduced air bubbles. Based on an analysis of Figs. 1 and 3, it can be found that the average bubble size decreases with an increasing amphiphile concentration as a result of a decrease in the surface tension and an increase in the foam viscosity. These two effects compensate for the less pronounced increase in the number of critical capillaries obtained for an increasing amphiphile concentration.²⁾

Therefore, the foam formation and resulting microstructures depend strongly on the initial amphiphile concentrations of the suspensions. Additional increases of the amphiphile concentration greatly increase the suspension viscosity, hindering the incorporation of air for the foam formation. Despite that the wet foams have nearly identical air contents, their average bubble sizes decreased from 250 to 50 μ m as the propyl gallate concentration increased from 0.001 M to 1 M. The foams with lower average bubble sizes also exhibited narrower bubble size distributions (Fig. 1). The concentration of the amphiphile also affected the suspension contact angles and surface tensions, which directly influenced the wet foam stability and bubble size and distribution (Fig. 3).

3.2. Contact Angle and Surface Tension

The contact angle of the particles in the suspension can also be tailored using the surface chemistry by adjusting the

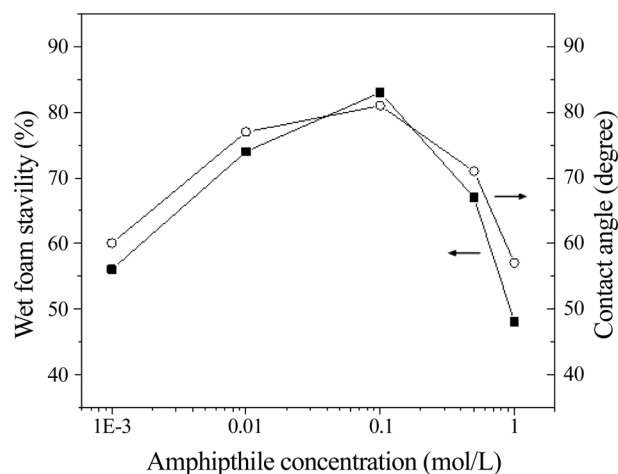


Fig. 1. Wet foam stability and contact angle with respect to the amphiphile concentration in the initial suspension.

fluid composition. The adsorption at the fluid interfaces occurs when particles are not completely wetted and when they exhibit finite equilibrium contact angles at the triple phase boundary. The equilibrium contact angle (θ) results from the balancing of all interfacial tensions. Oil (air)-in-water emulsions and foams result from contact angles below 90° and water-in-oil (air) emulsions and mists result from contact angles of 90° to 180° . Once the contact angle of the particles has been tuned, the emulsions and foams can be prepared by (a) mechanical shearing, (b) injection, or (c) internal phase transformations and chemical reactions that lead to aeration or emulsification. Stabilization has been reported to be achieved at intermediate contact angles of 40° to 86° in oil (air)-in-water emulsions and foams.⁹⁾

Fig. 2 illustrates that the wet foam stability that increases with an increase in the contact angle up to the 90° . Suspension contact angles of approximately 80 to 85° lead to higher stable foams. These foams do not shrink significantly after sintering, and have higher surface areas, and gain a porosity of approximately 82% after sintering (Fig. 3). This stability

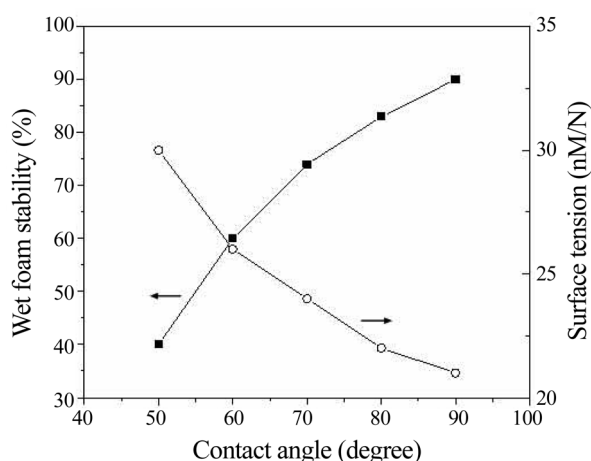


Fig. 2. Wet foam stability and surface tension with respect to the suspension contact angle prior foaming.

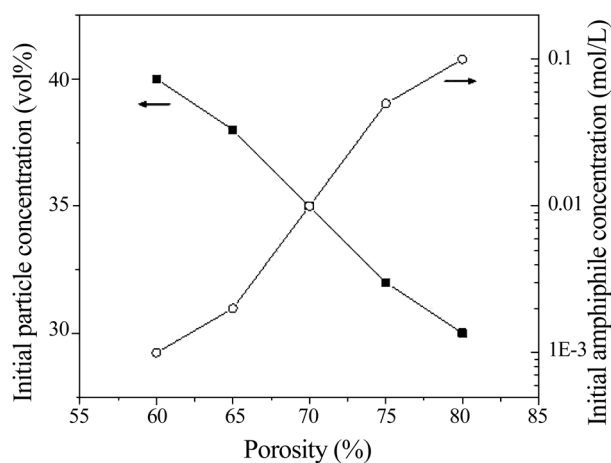


Fig. 3. Initial particle concentration and initial amphiphile concentration with respect to the porosity of the sintered foams.

toward Ostwald ripening, however, can be explained using the mechanical resistance of the outer particle layer against the shrinkage and/or expansion of the droplets and gas bubbles. The high stabilities rendered by the particles adsorbed at the surface of droplets and bubbles are also a key feature for the preparation of tailored materials from foams and emulsions.⁶⁾

Decrease in the surface tension results in the increase of porosity corresponding to higher contact angles of the suspension prior to foaming. Fig. 2 shows the effect of the contact angle on the wet foam stability and surface tension on the contact angle of the suspension prior to foaming. The decrease in the surface tension results from the increase in the amphiphile concentration which leads to stable foams. The graph demonstrates that surface tension of 21 mN/m, has a higher contact angle of 82° which results in higher stability in the foams. The amphiphile concentration after reaching the critical point of 0.1 M leads to a strong decrease in the surface tension, which in turn leads to instability in the foams. This reduction in surface tension is caused by a decrease in the total area of the highly energetic air-water interface and it explains the degree of hydrophobization achieved through the surface adsorption of the amphiphiles, which assists in stabilizing the foams and increasing the porosity.⁶⁾

3.3. Porosity and Microstructure

The high stability of the wet foams allows their direct drying in ambient air at room temperature. However, in order to avoid cracking, the wet foams must be slightly strengthened to overcome the capillary stresses and to avoid differential shrinkage within the drying foam. Cracking was avoided by coagulating the particles by the internal pH-shift reactions and adding additional additives to the suspension before foaming.^{2,11)} The subsequent drying and sintering resulted in closed cells. Fig. 3 shows the characteristics of these foams that achieved smaller average cell sizes of approximately 100-150 μm and exhibited either open or closed cells, even at high porosities. Fig. 3 also shows the effect of the particle and amphiphile concentration on the porosity of the sintered foams increase in both the components until the elevated point increases the porosity whereas further increase results in decreasing porosity. The change in viscosity of the suspension that increases with increasing content leads to a decrease in the foaming conditions and ultimately decreases porosity.⁸⁾

Fig. 4(a) and 4(b) show the microstructure of the sintered foam that was stable for several days under ambient conditions. The microstructure image of the porous ceramics under different amphiphile conditions showed different bubble sizes, distributions and hierarchies. Fig. 4(a) with an amphiphile of strength of 0.01 M showed larger bubble sizes and wide distributions whereas Fig. 4(b) with an amphiphile concentration of 0.1 M showed smaller average bubbles with narrow distributions. The comparative porosity analysis data (measured via Micromeritics) of both samples showed higher porosities upto 82% in Fig. 4(b) compared with Fig. 4(a) which showed 72% porosity. These data also verify the analysis that the sample porosi-

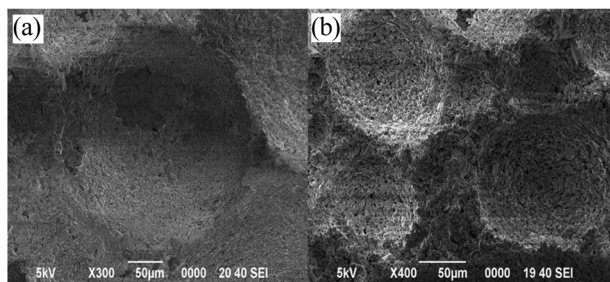


Fig. 4. Microstructure of the sintered foam with different amphiphile concentrations of (a) 0.01 M and (b) 0.1 M at 1200°C for 2 h.

ties are higher at certain critical points, which in this study were at 30 vol% particle concentration, with 0.1 M amphiphile strength showing a contact angle of 82°, a surface tension of 21 mN/m and average bubble size of 100-200 µm.

4. Conclusion

The remarkable resistance of the particle stabilized foams against coarsening has been attributed to the irreversible adsorption of the partially hydrophobic particles at the air-water interface. The adsorbed particles form a percolating armor along the air-water interface that mechanically withstands the lower pressures caused by the gas diffusion from the small bubbles during the Ostwald ripening. The resulting macroporous structures exhibited a total porosity of 82%. The foam cells were predominantly closed due to the air bubbles of the original wet foam being completely covered. According to this model, the final bubble size can be controlled by changing the suspension contact angle and surface tension. A scaling number containing these two variables was successfully employed to explain the effect of the suspension initial composition on the average bubble size and porosity of the sintered foams. An increase in the amphiphile concentration until the critical point of 0.1 M led to decrease in the surface tension and increase in the contact angle, which in turn led to foams with smaller average bubbles and higher porosities.

Acknowledgment

This research was financially supported by the Ministry of Education, Science Technology (MEST) and the National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation.

REFERENCES

1. U. T. Gonzenbach, A. R. Studart, E. Tervoort, and L. J. Gauckler, "Stabilization of Foams with Inorganic Colloidal Particles," *Langmuir*, 10983-88 (2006).
2. U. T. Gonzenbach, A. R. Studart, E. Tervoort, and L. J. Gauckler, "Tailoring the Microstructure of Particle-Stabilized Wet Foams," *Langmuir*, **23** [3] 1025-32 (2007).
3. N. D. Denkov, I. B. Ivanov, P. A. Kralchevsky, and D.T. Wasan, "A Possible Mechanism of Stabilisation of Emulsions by Solid Particles," *J. Colloid. Inter. Sci.*, **150** 589-93 (1992).
4. B. P. Binks, "Particles as Surfactants-similarities and Differences," *Curr. Opin. Colloid Interface Sci.*, **7** 21-41 (2002).
5. A. R. Studart, U. T. Gonzenbach, I. Akartuna, E. Tervoort, and L. J. Gauckler, "Materials from foams and Emulsions Stabilized by Colloidal Particles," *J. Mater. Chem.*, 3283-89 (2007).
6. T. S. Horozov, "Foams and foam films stabilized by solid particles," *Curr. Opin. Colloid Interface Sci.*, **13** 134-40 (2008).
7. T. N. Hunter, R. J. Pugh, G. V. Fanks, and G. J. Jameson, "A Role of Particles in Stabilizing Foams and Emulsions," *Adv. Colloid and Inter. Sci.*, **137** 57-81 (2008).
8. N. D. Denkov, I. B. Ivanov, P. A. Kralchevsky, and D. T. Wasan, "A Possible Mechanism of Stabilization of Emulsions by Solid Particles," *J. Colloid. Inter. Sci.*, **150** [2] 589-93 (1992).
9. B. Neirinck, J. Fransaer, O. V. der Biest, and J. Vleugels, "A Novel Route to Produce Porous Ceramics," *J. Eur. Ceram. Soc.*, **29** 833-36 (2009).
10. U. T. Gonzenbach, A. R. Studart, E. Tervoort, and L. J. Gauckler, "Ultrastable Particle-Stabilized Foams," *Angew. Chem. Int. Ed.*, **45** 3526-30 (2006).
11. D. K. Lim and E. T. Kang, "Porous Materials from Waste Bottles by Hydrothermal Treatment (in Korean)," *J. Kor. Ceram. Soc.*, **46** [3] 275-281 (2009).