

Stabilization of nano-particles in concentrated colloidal suspension to porous ceramics

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This study presents a novel method to study the stabilization mechanism of wet foams in concentrated colloidal suspension. The thermodynamic instability of wet foam bubbles in water due to the large and highly energetic interfacial area is the main challenge of processing such foams from colloidal suspension. Smaller bubbles under pressure diffuse into larger bubbles. This is known as Ostwald ripening, and it results in coarsening of the wet foam. Hence, the bubble size distribution broadens. To optimize the bubble size and the stability of wet foam, the adsorption free energy and Laplace pressure of nano-particle stabilized colloidal suspensions are investigated. Porous ceramics with more than 90% wet foam stability can be prepared easily with this novel approach. The sintered foam shows a particle free energy of $1.7 \times 10^8 \sim 3.2 \times 10^8$ kTs and pressure difference of 20 mPa to 25 mPa for colloidal Al_2O_3 and SiO_2 particles with particle size of 40 nm and 20 nm respectively.

Key words: Surface modification, Ostwald ripening, Adsorption free energy, Laplace pressure, Wet foam stability, Porous ceramics.

Introduction

Porous ceramics are of great interest due to their numerous potential applications in catalysis, adsorption and separation, as well as in the filtration of molten metals and hot gases, the refractory insulation of furnaces, and hard tissue repair and engineering. Porous ceramics show low thermal conductivity, excellent chemical resistance, and unique porous microstructure due to their interconnected structure of opened and closed pores [1-3]. Here we prioritize on the direct foaming technique, one of the main fabrication routes to porous ceramics in which a gaseous phase is incorporated into a ceramic suspension.

Because of the large and highly energetic interfacial area of air and water, the wet foam bubbles of the colloidal suspensions create a thermodynamically unstable state. The liquid foams collapsed due to the combined actions of such destabilization mechanisms like drainage, coalescence & Ostwald ripening. Several short-chain amphiphilic molecules and biomolecules such as lipids and proteins acts as surface modifiers by slowing down the coalescence and disproportionation of bubbles by adsorbing at the air bubble surface and reducing the air-water interfacial energy [4]. This process is known as in-situ hydrophobization which allows preparation of ceramic foams containing high concentration of partially-hydrophobized particles with long term stability [5].

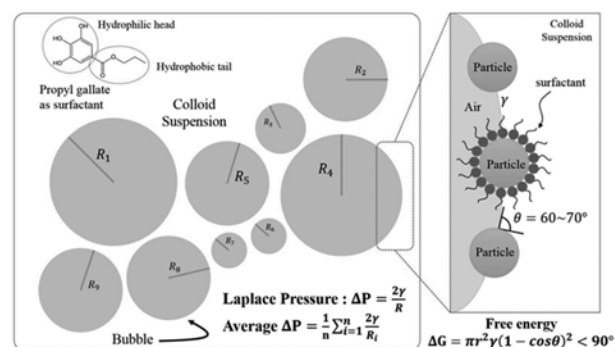


Fig. 1. Estimation of Laplace pressure and free energy from colloidal suspension.

Porous bulk materials exhibiting closed or open pores can be produced upon drying and sintering which allow it to be used for various practical applications.

However, the thermodynamic instability of wet foams due to difference between the pressure acting on gas bubbles of distinct sizes (R) leads to bubble coarsening and Ostwald ripening. This occurs because of the steady diffusion of gas molecules from smaller to larger bubbles over time, followed by the broadening of the bubble size distribution [6-7]. Eventually, the liquid foam collapses due to the combined actions of these destabilization mechanisms.

Surfactant and bio-molecules adsorbed at the gas-liquid interface can prolong the life span of newly formed bubbles by decreasing the interfacial tension γ [8-9]. The use of short chain amphiphiles to improve particle wettability as shown in (Fig. 1) is a general and versatile approach for the surface modification of a wide

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range of ceramic and metallic materials [10-12]. The theory of stabilization [13] was used in this experiment to produce porous ceramics, and was described with different variables.

Experimental Procedure

Materials

The experiment was carried out using high-purity alumina (α - Al_2O_3 , $d_{50} \sim 40$ nm, >99.99%, MTI Richmond, CA, USA) and SiO_2 (SiO_2 , $d_{50} \sim 20$ nm, >99%, MTI Richmond, CA, USA). The other chemicals used in this experiment are deionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China).

Suspension preparation

Suspensions containing propyl gallate as an amphiphile were prepared by the stepwise addition of alumina powder to an aqueous mixture of 0.01 M NaOH and 0.01 M propyl gallate. The solid loadings and pH of the suspensions were initially fixed at 50 vol.-% and 6.7, respectively. Homogenization and de-agglomeration were performed via ball-milling for at least 48 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 (2 wt.-% to Al_2O_3) in the final suspension. The solid loading of final suspension was fixed at 30 vol.-% by adding de-ionized water.

Contact angle and surface tension

The pendant drop method (KSV Instruments Ltd, Helsinki, Finland) was used to measure the contact angles and surface tensions of the suspensions. Depending on the contact angle and surface tension of the suspension, the drop volume was set to a constant value within the range of 5-10 μL .

Foaming, drying, and sintering

The foaming of 150 mL suspensions was carried out using a household hand mixer (150 watt, Super Mix, France) at maximum power level for 5-10 minutes as shown in (Fig. 2). The average wet bubble size was measured by analyzing optical microscope images using the software Linear Intercept (TU Darmstadt, Germany). The optical microscope (Somtech Vision, South Korea) in transmission mode was connected to a digital camera. The bubble sizes were measured using linear intercepts. The average bubble size was determined by the analysis of 100 bubbles in a composition. Wet foams were dried at 20 °C-25 °C for 48 hr. The dried foams were sintered in a super kantel furnace (max 1650 °C) at 1300 °C for 1 hr. The heating rate was set to 1 °C/min, and the cooling rate was 3 °C/min.

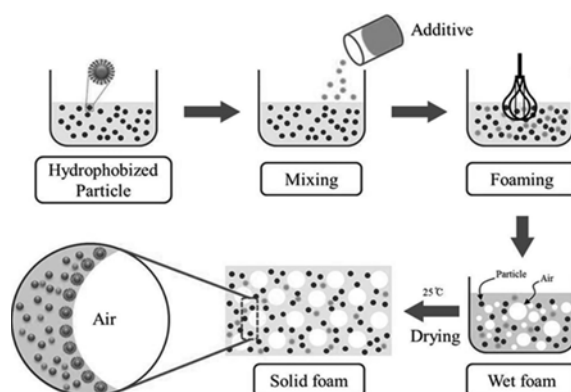


Fig. 2. Schematic diagram of the direct foaming technique.

Results and Discussion

Controlling contact angles of the particles at the interface is important, since the angles modify the wettability of the particles by changing their hydrophobicity, as shown in (Fig. 3). Generally, lower contact angles improve the wettability. Different contact angles can be achieved by imparting different hydrophobic molecules commonly known as surfactants.

It is shown from the (Fig. 3) that the average contact angle of the $d_{50} \sim 40$ nm Al_2O_3 suspension decreased from 84° to 67° with the increased SiO_2 content (1.0 mole ratios in the Al_2O_3 suspension). Also, the increasing SiO_2 content produced lower adsorption free energy due to the higher inter-particle attraction, increasing the viscosity. The suspensions with mol ratios of SiO_2 between 0.25 and 0.5 in the suspension show higher levels of attachment energy, resulting in highly stable foam in the sintered porous ceramics. Also, contact angle of around 70° to 75° for the nanoparticle suspension leads to better wet foam stability, and can give surface tensions of 21-33 $\text{mN}\cdot\text{m}^{-1}$. The required partial hydrophobization of the particles occurs at this point, which leads to porous ceramics with higher porosity.

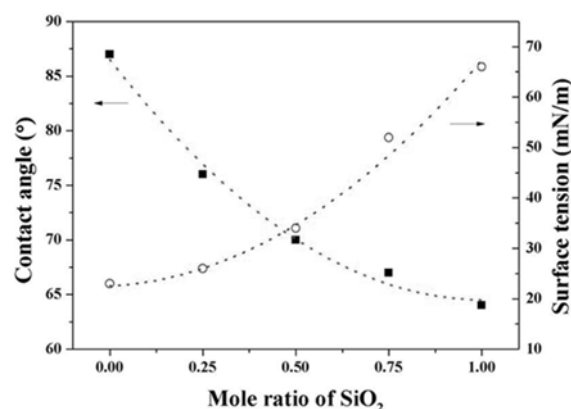


Fig. 3. Contact angle and surface tension of colloidal suspension with respect to different mole ratio of SiO_2 .

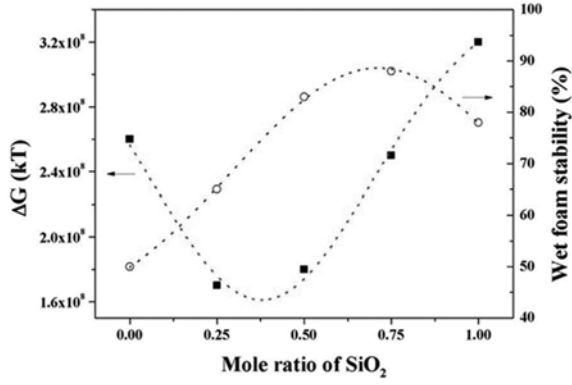


Fig. 4. Free energy and wet foam stability with respect to the different mole ratio of SiO₂.

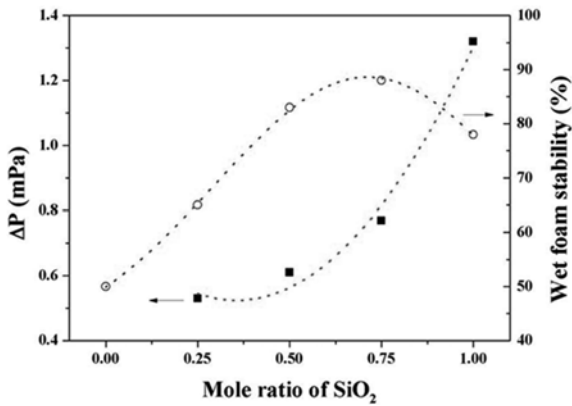


Fig. 5. Laplace pressure and wet foam stability with respect to the different mole ratio of SiO₂ content

The energy of attachment or free energy gained (ΔG) by the adsorption of a particle of radius r at the interface can be calculated using the following equations where θ is contact angle and γ is surface tension:

$$\Delta G = \pi r^2 \gamma_{\alpha\beta} (1 - \cos \theta)^2 \quad 1 [14]$$

According to 'equation (1)', G (the Gibbs free energy) is greatest when θ is 90°; however, the foam stabilization of particles readily occurs when θ is between 50° and 90°. (Fig. 4) shows the change in the adsorption energy corresponding to the different mole ratio of SiO₂ content used to stabilize the suspension. An Al₂O₃ loading of 30 vol.-% in the suspension was taken as a standard, and experiments were performed with 0.01 molL⁻¹ amphiphiles for stabilization of the particles. The calculations show that the energy level decreases with the nanoparticle size and with increase in SiO₂ content. However after the middle value (0.75) of the SiO₂ loading, the van der Waals attraction force between the particles gradually increases, forcing the suspension to destabilize and finally decrease the wet foam stability from 87% to 68%. A higher energy of adsorption of 1.7×10^8 kTs could be achieved in the initial suspension without SiO₂ content. The adsorption free energy decreases with the increasing concentration.

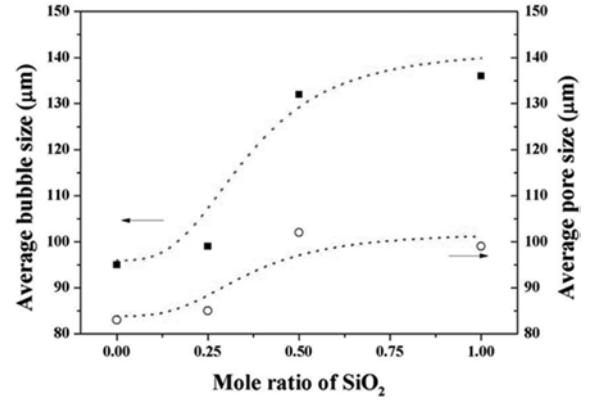


Fig. 6. Bubble size and pore size with respect to the SiO₂ content of the wet foam before and after sintering at 1300 °C for 1 hour.

Higher contact angle of 62° to 75° with a lower interfacial energy of 1.7×10^8 kTs were seen at SiO₂ mole ratio of 0.25 giving an interfacial tension of 42 to 45 mNm⁻¹.

The pressure acting on gas bubbles in a colloidal suspension can be described by the Laplace pressure ΔP as follows:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) \quad 2 [15]$$

The Laplace pressure (N/m²) is the pressure difference between the inner and outer side of a bubble or droplet. For spherical bubble of radius R and gas-liquid interfacial energy ΔG , the Laplace pressure ΔP is given by $2\gamma/R$ (Fig. 1). (Fig. 5) shows the wet foam stability corresponding to the pressure exerted by the bubbles (Laplace pressure) with respect to the different mole ratio of SiO₂ content. The Laplace pressure increases with the increase in SiO₂ concentration. This behavior can be attributed to the fact that high SiO₂ content requires large volume of water in the suspension which subsequently lowers the outer pressure of the bubble. The wet foam stability suddenly decreases due to high Laplace pressure when the mole ratio of SiO₂ reached at 0.60. The wet foams were stable at the pressure difference between 20 to 25 mPa, which corresponds to the SiO₂ mole ratio content of 0.25 to 0.50. The stability increased to more than 80% at a SiO₂ mole ratio of 0.75.

(Fig. 6) shows the bubble size of the wet foam and the pore size by the sintered ceramics formed after the foaming of the particle stabilized suspension and heat treatment respectively. The average bubble size for these types of stabilized foams was 98 to 140 μm. The required partial hydrophobization of the particles occurs at this point, which leads to porous ceramics with porosity greater than 80% and pore size of about 108 μm after sintering at 1300 °C for 1 hour.

The microstructures are described in (Fig. 7), where tailored, open and closed, interconnected pores can be seen. Also, it can be seen that the larger and smaller

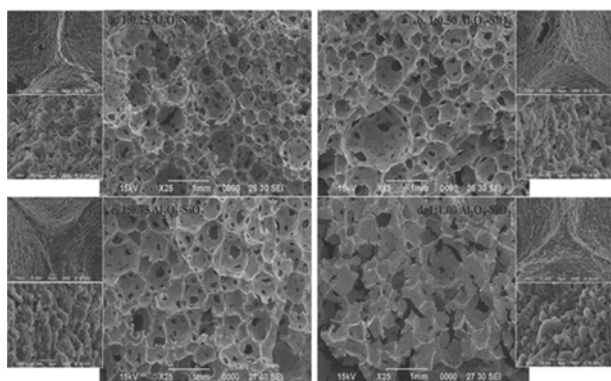


Fig. 7. Microstructures and thin film (inner cell) of porous ceramics sintered at 30 vol.-% Al_2O_3 with respect to the different mole ratio of SiO_2 content.

pores are uniformly distributed. In (Fig. 7, a through d), different compositions of $\text{Al}_2\text{O}_3/\text{SiO}_2$ with well-developed and narrow pore size distribution can be seen. It shows a hierarchical pore distribution with porosities up to 80% from larger to smaller pores and thick struts (films in wet foams). It leads to produce more stable foams sintered to form porous ceramics with high mechanical strength.

Conclusions

In conclusion, this study showed that the stability of the ceramic foam is directly related to the surface tension of the colloidal suspension, which helps to tailor the free energy and Laplace pressure with a corresponding interfacial contact angle. A stabilizing point was obtained for the production of the porous ceramics, which is directly related to the solid content and particle sizes. A wet foam stability of more than 90% was established with the particle free energy of 4.0×10^8 to 2.0×10^4 kTs and pressure difference of 20 mPa to 25 mPa for colloidal Al_2O_3 and SiO_2 particles with particle size of 40 nm and 20 nm respectively.

Acknowledgments

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