

Effect of surfactant on adsorption free energy and Laplace pressure of wet foam stability to porous ceramics

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This is a novel approach for the study of the effect of different surfactant concentration with the maximum wet foam stability of 85%. The production of silica foams with varied amphiphile concentration was done using wet foam technique at a specific range of pH. The wet foams were dried at room temperature and sintered with improved porosity, were found to be friable in nature, corresponding to the particle's free energy of 1.7×10^8 kTs and pressure difference of 1.0 mPa for colloidal SiO₂ particles with average diameter of 3.5 μ m. The roughly distributed granular pore structures were found in the micro structural examinations of the sintered foams which were done using optical and scanning electron microscopy where the agglomeration of the bubbles occurs due to Ostwald ripening at 0.10(M) Hexylamine concentration with 30 vol% of solid loading. The porous microstructure shows interconnected cells in the size range of 100 to 300 μ m.

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

Introduction

Advanced ceramic materials play a key role in the fields of modern technologies such as communication and information technology, energy and environmental technology, transportation and production technology as well as life sciences. Ceramic manufacturing usually involves processing of inorganic powders into desired component shape, followed by densification at elevated temperatures via solid- or liquid- state engineering [1]. The Polymeric sponge method [2-4] and direct foaming method [2, 5, 6] are the two representative methods commonly utilized to prepare silica based ceramic foams. In direct foaming methods, porous materials are produced by incorporating air into a suspension or liquid media, which is subsequently set in order to keep the structure of the air bubbles created. In most cases, the consolidated foams are afterwards sintered at high temperatures to obtain high strength porous ceramic [7]. The stabilization of the air bubbles incorporated within the suspension in this method is very critical and involves the use of either surfactant [8].

The surfactant films can reduce surface tension, increase surface viscosity and create electrostatic force to prevent foam from collapsing. The pH, contact angle and surface tension of the colloidal suspension are important parameters for its stability. The difference in Laplace pressure between the bubbles of different sizes

leads to Ostwald ripening or other disproportionation which is more difficult to overcome. Wet foam's stability is also related to the degree of hydrophobicity achieved from the surfactant, which replaces part of the highly energetic interface area and lowers the free energy of the system [9].

This study presents a versatility of wet foam stabilization fabricating SiO₂ based porous ceramics using the simple method of direct foaming. The silica particles get partially hydrophobized by the addition of a surfactant, Hexylamine with optimized chain length. The stabilization of the foams in wet state occurs when the negatively charged surfaces of silica particles get coated with the positively charged hydrophobic end of Hexylamine making the molecule partially hydrophobic as shown in fig. 1. But with the consequent increase in the amphiphile concentration their adsorption in the particle surface increases which leads to the reduction

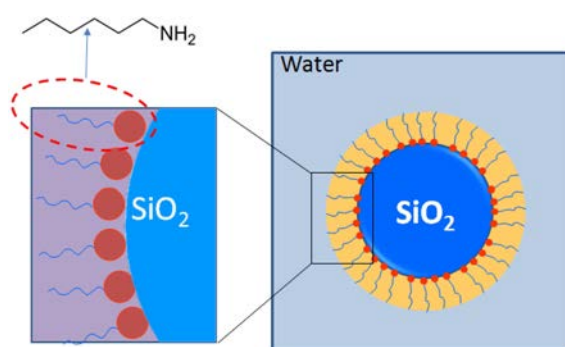


Fig. 1. Partially hydrophobized SiO₂ particle produced by adding Hexylamine as a surface modifier.

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of the void spaces. As a result reduces air flow due to the increase in viscosity and the wet foam stability decreases.

Experimental Procedure

Raw materials

The raw materials used in this study include high-purity Silica powder (d_{50} -3.5 μm , Junsei Chemicals, Japan), de-ionized water, Hexylamine (Alfa Aesar, Seoul, Korea), hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan) and sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan).

Processing

Preparation of suspension and optimization of hexylamine content

The suspensions were prepared by addition of silica powder with de-ionised water through homogenization and de-agglomeration using zirconia balls (10 mm in diameter-2 : 1 ratio of balls to powder), ball-milling for at least 24-36 hours. The solid loadings were adjusted to 50 vol% with a specific pH range of the suspensions of 9.9-10.5. The final solid content of the suspensions were dropped to 30 vol% as per the requirement of the particle concentration. The Hexylamine was adjusted to the different required concentrations in the final suspensions with continuous stirring. The pH of the suspensions were adjusted within the range of 9.9-10.5 with the addition of required amounts of (0.1N) NaOH or (0.1N) HCl.

Measurement of contact angle, surface tension and bubble size

The contact angles and surface tensions of the suspensions were measured using pendant drop method (KSV Instruments Ltd, Helsinki, Finland). Silica suspensions were prepared through the drop-wise addition of Hexylamine to generate solid loadings of 30 vol% silica. Depending on the suspension contact angle and the surface tension the drop volume varied between 5 and 10 μl .

Foaming, drying, sintering and analysis

The foaming of 100 ml suspension was performed using a household mixer (150 watt, Super Mix, France) at full power for 5 to 10 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 and measured using linear intercepts. Adsorption Free Energy and Laplace Pressure including the wet foam stability were calculated from the results obtained. Wet samples were dried at 20-25 $^{\circ}\text{C}$ for 24-48 hrs. The dried foams were sintered in an electric muffle furnace at 1250 $^{\circ}\text{C}$ for 1 hr with the rate of heating and cooling at 1 $^{\circ}\text{C}/\text{min}$ and 3 $^{\circ}\text{C}/\text{min}$ respectively. The micro

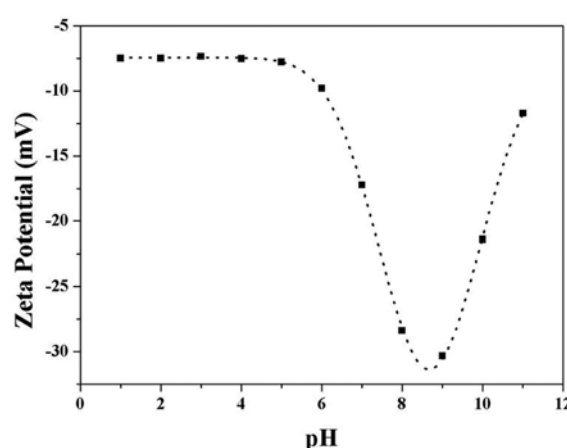


Fig. 2. Zeta Potential (mV) of SiO_2 with respect to pH.

structural examinations of these samples were done using scanning electron microscope (SEM).

Results and Discussion

Zeta potential

The zeta potential is the electric potential in the interfacial double layer (DL) at the location of the slipping plane versus a point in the bulk fluid away from the interface. In other words, zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. It is used to determine the exact pH range of the compound. Fig. 2 infers that the exact pH range for SiO_2 should be between 9.9-10.5 which have been proved to be the most suitable condition for performing the experiment.

Contact angle and surface tension

Ceramic particles can achieve any contact angle by reacting or adsorbing hydrophobic molecules on their surfaces as it depends on surface chemistry, roughness, impurities, particle size and the composition of the fluid phases. [10] Controlling particles' contact angles at the

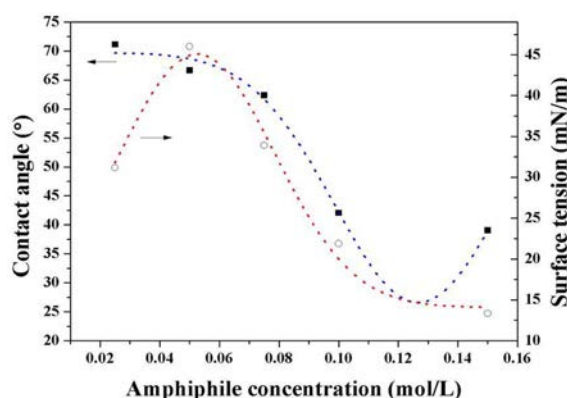


Fig. 3. Contact angle and surface tension against amphiphile concentration (mol/L) of SiO_2 .

interface is important for the determination of their degree of hydrophobization. The average contact angle of the d_{50} -3.5 μm SiO_2 suspension increased with the increase Hexylamine content. In fig. 3 the suspension of 0.05M of Hexylamine content were found to be highly stable with a higher level of surface tension resulting in highly stable foams to sintered porous ceramics. It can also be proved that contact angle of around 64° for micro-particle suspension leads to better wet foam stability which further increased by micro particle suspension can give the surface tension of 45 mN/m. The required partial hydrophobization of the particles occurs at this point which leads to the porous ceramics with higher porosity.

$$\Delta E = \pi r^2 \Gamma_{\alpha\beta} (1 - \cos \theta)^2 \text{ for } \theta < 90^\circ \quad (1)^{11}$$

Where, θ is the contact angle of the suspension and $\Gamma_{\alpha\beta}$ is the surface tension.

The figure depicts that the energy level increases with the corresponding particle size and with increased amphiphile concentration. But after the middle value 0.05M Hexylamine concentration loading the particles start attracting each other, resulting in the higher attracting Van der Waals force, forcing the suspension to destabilize and finally decrease the wet foam stability from 87 to 62% with the adsorption free energy of 1.6×10^8 kTs.

Fig. 4(b) shows the wet foam stability corresponding to the pressure exerted by the bubbles (called Laplace pressure, ΔP), of the wet foams formed with respect to the particle size and concentration which can be calculated by the following equation-

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} \text{ (For spherical bubble)} \quad (2)^{12}$$

where, ΔP = Laplace pressure(N/m²), is the difference between the inner and outer surface of a bubble or

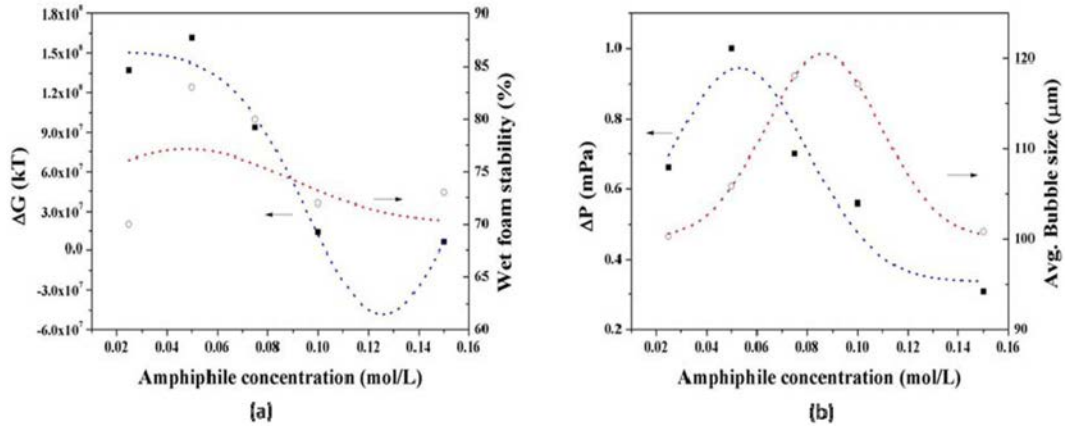


Fig. 4. (a) Adsorption free energy vs. wet foam stability (b) Laplace pressure vs. bubble size, of the initial 30 vol% SiO_2 suspension (3.5 μm) with respect to different amphiphile concentration.

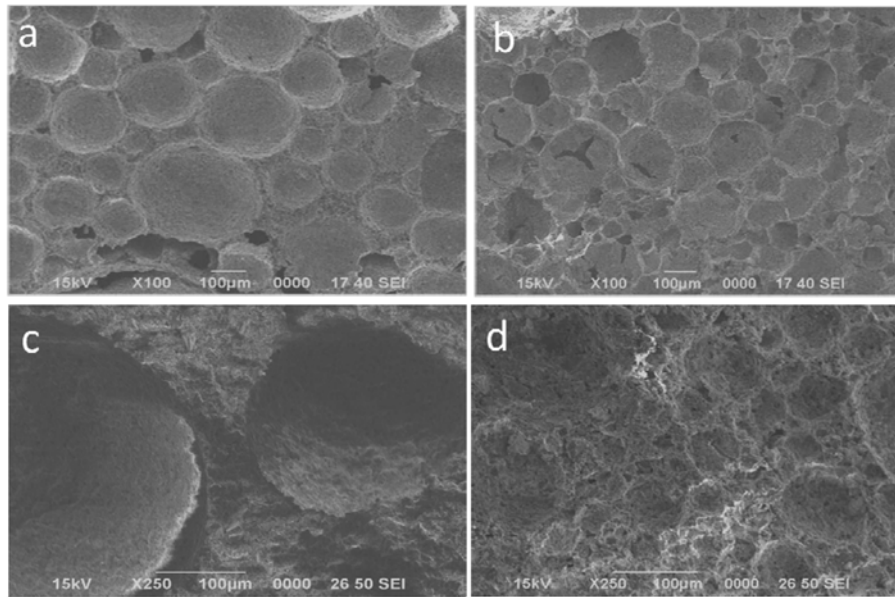


Fig. 5. Microstructures of foams of SiO_2 sintered at 1250 $^\circ\text{C}$, 30 vol% SiO_2 suspension with different Hexylamine: (a) 0.025(M), (b) 0.05(M), (c) 0.10(M) and, (d) 0.15(M) respectively.

droplet, the effect of which is caused by the surface tension μ (mN/m) of the interface between liquid and gas, R_1 and R_2 = radius of curvature for ne ellipse are taken into consideration. However, for the spherical shaped bubbles R_1 and R_2 are equation so we used the second formula for the calculation of the Laplace pressure.

The difference in pressure kept increasing until the maximum, and the stability increased until SiO₂ concentration of 30 vol%. The pressure increased with increase in Hexylamine content as the Laplace pressure is inversely proportional to the bubble size. The wet foams were stable at the pressure difference of 1.0 mPa, which corresponds to the Hexylamine content of 0.05M; the further increase in the loadings resulted in a lower difference of pressure, resulting in lower stability.

The bubble size of the particles decreases with the increase in the amphiphile concentration. The pore size by thin film or struts formed after the foaming of the particle stabilized suspension as well as the bubble size of the suspension including sintering is described in terms of attractive and repulsive interactions between bubbles. Single or multi layers of modified particles are observed on the thin films, which maintain stability of the films to withstand the change in the pressure between the bubbles. Electrostatic forces, steric repulsions force or by ligand exchange reactions can overcome the Van der Waals force [11]. By using surfactants adsorbed at the interface, the process can be slowed down, which can decrease the interfacial energy. The degree of hydrophobicity achieved from the surfactant is related to the wet foam stability, which leads to an apparent reduction in the surface tension of the suspension by replacing part of the highly energetic interface area and lowering the free energy of the system [13, 14].

The microstructures are described in fig. 5(a) and (b) have more well-developed and smooth surface along with narrow pore size distribution whereas the pore size is found to be correspondingly decreasing as the average bubble size in fig. 4. Fig. 5(c) implies the agglomeration of the bubbles as per the experimental results the wet foam stability gets reduced at this concentration due to Ostwald ripening. Fig. 5(d) shows thick struts showing a hierarchical pores distribution from larger to smaller pores and struts (films in wet foams) which led to higher stable foams sintered to porous ceramics.

Conclusions

The free energy and the Laplace pressure can be calculated corresponding contact angle interface, whereas the stability of the ceramic foam is directly related to the surface energy of the colloidal suspension. We conclude that a stabilizing point was obtained for the production of the porous ceramics and explained that it can be tailored with the solids content, which is directly related to the free energy and Laplace pressure of 1.0 mPa, corresponding to the wet-foam stability of sintered porous ceramics. The wet foam stability maximum of around 87% was established corresponding to the particles free energy of 1.6×10^8 kT at a amphiphile concentration of around 0.05M.

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