I O U R N A L O F

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Particle-stabilized wet foams to porous ceramics by direct foaming

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This study presents a versatile method for the production of silica foams with different particle concentration that have wet foam stability above 80%. The foams were produced by using a direct foaming method with inorganic particles (SiO₂) and Hexylamine, a short chain amphiphile, at a specific range of pH through the in-situ hydrophobization mechanism. The wet foams were finally dried at room temperature and then sintered, exhibiting free energy of 2.5×10^8 kTs and pressure difference of 0.8 mPa for colloidal SiO₂ particles with average diameter of $3.5 \,\mu$ m. Microstructural examinations of the wet and the sintered foams were performed through the use of optical and scanning electron microscopy where the decrease in pore size was observed to be related to an increase in particle concentration among the interconnected pores.

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

Introduction

Porous ceramic foams are widely known to have high specific and chemical resistance, good insulating characteristics, high permeability, high refractoriness, and long life in severe environments due to their high porosity and well developed three dimensional network surface pore structures [1]. Wet foams from colloidal suspensions are routinely used as end or intermediate products in many different areas ranging from cosmetics and food to oil recovery and materials manufacture [2]. The thermo dynamical instability of the colloidal suspension is due to their large air-water interfacial area as well as high overall free energy. In order to reduce this free energy of wet foams the surfactants are used by lowering the air-water interface tension. Nevertheless, surfactants can be easily desorbed from the interface because their energy of attachment to the interface is comparable to thermal energy (few kTs, kbeing Boltzmann's constant and T the temperature). As a result, destabilization mechanisms such as bubble coalescence and disproportionation (Ostwald ripening) cannot be completely prevented in particle-stabilized foams which leads to bubble coarsening over time [3-5].

The representative methods utilized commonly to prepare silica based ceramic foams are, the polymeric sponge method, the replica technique, the sacrificial template method and the direct foaming method, [6-10] where the air is directly incorporated into the colloidal

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suspension. These foams have also been widely used for a variety of applications in light-weight thermal protection systems. The stabilization of the air bubbles incorporated within the suspension in this method is very critical and involves the use of Hexylamine as surfactant [11]. Surfactants can reduce surface tension, increase surface viscosity, and create electrostatic force to prevent the foam from collapsing. The pH, contact angle, and surface tension of the colloidal suspension are important parameters for its stability. The stability of wet foam is also related to the degree of hydrophobicity achieved by the surfactant that replaces part of the highly energetic interface area and lowers the free energy of the system [12].

The degree of particle hydrophobization depends on the amount of adsorbed amine and the length of the hydrophobic tail [13]. To extend this approach to different types of inorganic particles, one has to deliberately select amphiphilic molecules exhibiting a short hydrophobic tail (two to seven carbons) combined with a head group that is able to adsorb on each specific particle surface. Therefore, the choice of the amphiphile head group highly depends on the surface chemistry of the particle involved [14].

In this study we prepared pure silica based suspension using Hexylamine as surface modifier to partially hydrophobize the SiO_2 particles. The pH of the initial suspension is kept within the range of 9.9-10.5 as per the records of the zeta potential. The surface tension of the suspension is calculated by pendant drop method along with the contact angle. The adsorption free energy and the laplace pressure are calculated from equation (1) and (2). The wet foam stability of the

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dried foam is measured which are then sintered in a muffle furnace at $1250 \,^{\circ}$ C for 1 hr.

Experimental Procedure

Raw materials

The raw materials used in this study include highpurity Silica powder ($d_{50} \sim 3.5 \mu m$, 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).

Preparation of suspension and optimization of hexylamine content

The suspensions were prepared via homogenization and de-agglomeration of silica powder in de-ionized water with the use of zirconia balls (10 mm in diameter, -2:1 ratio of balls to powder), and subsequent ballmilling for at least 24-36 hours. The solid loading and pH of the suspensions were initially fixed at 50 vol% and 9.9-10.5, respectively. Hexylamine was adjusted to the required concentration (0.05 M) in the final suspension with continuous stirring to hydrophobize the SiO₂ particle as shown in Fig. 1. Here the contact angle as well as the surface tension was found to be maximum at 0.05(M) of Hexylamine concentration. As a result the wet foam stability was highest too at this point. The final solid content of the suspensions were lowered to a different vol% as per the requirements of the particle concentration. The pH of the suspensions were adjusted within the range of $9.9 \sim 10.5$ by adding the required amounts of (O.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 the pendant drop method (KSV Instruments Ltd, Helsinki, Finland). Silica suspensions were prepared through the drop-wise addition of Hexylamine to generate solid loadings of



Fig. 1. Contact angle and surface tension with respect to amphiphile concentration of SiO_2 suspension.

30 vol% of silica. Depending on the suspension contact angle and the surface tension, the drop volume varied between 5 and 10 μ l.

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 were 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 °C for 24-48 hrs. The dried foams were sintered in an electric muffle furnace at 1250 °C for 1 hr with the rate of heating and cooling at 1 °C/min and 3 °C/min, respectively. The micro structural examinations of these samples were done by using a scanning electron microscope (SEM).

Results and Discussion

Contact angle and surface tension

Ceramic particles can achieve any contact angle by reacting or adsorbing hydrophobic molecules on their surfaces as adsorption depends on surface chemistry, roughness, impurities, particle size, and composition of the fluid phases [15]. This study presents a novel approach for achieving wet foam stabilization by fabricating silica based porous ceramics by using the simple method of direct foaming. The silica particles get partially hydrophobized with the addition of Hexylamine, an amphiphile, with optimized chain length as shown in Fig. 2. The negatively charged surfaces of silica particles get coated with the positively charged hydrophobic end of Hexylamine, making the molecule partially hydrophobic and leading to the stabilization of the foams in the wet state. Controlling the particles' contact angles at the interface is important in order to



Fig. 2. Schematic representation of partially hydrophobized SiO_2 particle produced by adding Hexylamine as a surface modifier.



Fig. 3. Contact angle vs. surface tension of the initial SiO_2 suspension (3.5 μ m) with 0.05 M Hexylamine with respect to particle concentration.



Fig. 4. Adsorption free energy vs. wet foam stability of the initial SiO_2 suspension (3.5 μ m) with 0.05 M Hexylamine as a function of particle concentration.

determine the degree of hydrophobization. The average contact angle of the d_{50} –3.5 µm SiO₂ suspension increased with the increase in SiO₂ content.

In Fig. 3 the suspensions with content between 25 and 30 vol% of SiO₂ were found to be highly stable with a higher level of surface tension resulting in highly stable foams to sintered porous ceramics (see Fig. 3 & 4). It can also be proved that the contact angle of around 67-77 ° for micro-particle suspension leads to better wet foam stability and this further increase by micro-particle suspension can give the surface tension of 40-47 mN/m. The required partial hydrophobization of the particles occurs at this point to produce porous ceramics with higher porosity.

Fig. 4 shows the change in the adsorption free energy (E) corresponding to the SiO_2 content and different particle concentration used to stabilize the suspension. This can be calculated by using the following equation-

$$\Delta E = \pi r^2 \ \Upsilon_{\alpha\beta} \ (1 \text{-}\cos \theta)^2 \text{ for } \theta < 90^{\circ} \tag{1}^{16}$$

Where, θ is the contact angle of the suspension, r is the radius of the solid particle and $\Upsilon_{\alpha\beta}$ is the surface



Fig. 5. Laplace pressure vs. wet foam stability of the initial SiO_2 suspension (3.5 μ m) with 0.05 M Hexylamine with respect to particle concentration.

tension.

It depicts the increase in energy level with the corresponding particle concentration and with an increase in SiO₂ content. However, after the middle value 25-30 vol% of the SiO₂ loading the particles start attracting each other, and this result in higher attraction through the Van der Waals force, forcing the suspension to destabilize and finally decrease the wet foam stability from 90 to 77% as well as the adsorption free energy 2.0×10^8 -2.5 × 10^8 kT.

Fig. 5 shows pressure exerted by the bubbles (called Laplace pressure, ΔP) correspondence with the average bubble size. Taking into account the particle concentration, it can be calculated by using the following equation-

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2}\right) \tag{2}^{17}$$

Where, γ is the surface tension of the particles, and R₁ and R₂ are the radii of the bubbles in the wet state. The difference in pressure kept increasing until the maximum was achieved, and the stability increased until the SiO₂ concentration reached a level of 30 vol%. The pressure increased gradually with an increase in SiO₂ content since the Laplace pressure is inversely proportional to the bubble size (see Fig. 6). The wet foams were stable at a pressure difference between 0.8 and 1.3 mPa with the average bubble size of 50 µm and the wet foam stability of more than 80%, and this corresponds to the SiO₂ content of 25-30 vol%.

Porosity, pore morphology and size distribution of the micro structures can be tailored by the processing route used for the production of porous ceramics by the process of particle stabilized method of direct foaming [18]. The stability of the wet foam bubbles against collapse is achieved by setting the foam through the addition of gelling agents or the condensation of metal hydroxides and alkoxides [19-21]. In Fig. 6 we find that the pore size reduces with respect to the bubble size due to the shrinkage of the bubbles during the



Fig. 6. Average bubble size vs. average pore size of the wet and dried SiO_2 foam with respect to particle concentration of the suspension.



Fig. 7. Microstructures of SiO₂ porous ceramic sintered at 1250 °C for 1hr, 0.05 M Hexylamine with different SiO₂ content: (a) 20 vol%, (b) 25 vol%, (c) 30 vol% and (d) 35 vol%, respectively.

sintering process. At 35 vol% particle concentration we can find the Laplace pressure (see Fig. 5) to be too high which denotes that the pressure between the two bubbles is more which forces them to agglomerate as a result leads to Ostwald ripening. This is shown in the microstructures where the shrinkage of the pores occurs due to the sintering process (see Fig.7(d)).

The microstructures are described in Fig. 7, where the interconnected pores are seen within all the structures with uniform distributions of pore sizes. Fig. 7(a) shows a more developed and smoother surface along with narrow pore size distribution whereas in Fig. 7(b) and 7(c) the bubble size is found to correspondingly decrease. Fig. 7(d) implies that the abnormal growth of the bubbles due to Ostwald ripening, as per the experimental results of the wet foam stability, is reduced at 35 vol% concentration of SiO₂. The analysis showed a hierarchical pores distribution from larger to smaller pores and struts (films in wet foams) which led to higher stable foams sintered to form porous ceramics with gradually decreasing pore size.

Conclusions

The free energy and the Laplace pressure can be calculated in a manner corresponding to the 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 porous ceramics, and we explained that it can be tailored with the content of the solids, which in turn is directly related to the free energy and Laplace pressure in the range of 0.8 to 1.3mPa, that correspond to the wet-foam stability of sintered porous ceramics. The wet foam stability maximum of around 80% was established to correspond to the particle's free energy of 2.0×10^8 - 2.5×10^8 kT at a particle concentration of around 25-30 vol%. The microstructures prove the decrease in the pore size with the increase in the particle concentration as well as Ostwald ripening is seen in the 35 vol% concentration where the bubbles are found to get agglomerate.

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