Effect of Process Conditions on the Microstructure of Particle-Stabilized Al₂O₃ Foam

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Abstract Al₂O₃ foam is an important engineering material because of its exceptional high-temperature stability, low thermal conductivity, good wear resistance, and stability in hostile chemical environment. In this work, Al₂O₃ foams were designed to control the microstructure, porosity, and cell size by varying different parameters such as the amount of amphiphile, solid loading, and stirring speed. Particle stabilized direct foaming technique was used and the Al₂O₃ particles were partially hydrophobized upon the adsorption of valeric acid on particles surface. The foam stability was drastically improved when these particles were irreversibly adsorbed at the air/water interface. However, there is still considerable ambiguity with regard to the effect of process parameters on the microstructure of particle-stabilized foam. In this study, the Al₂O₃ foam with open and closed-cell structure, cell size ranging from 20 µm to 300 µm having single strut wall and porosity from 75% to 93% were successfully fabricated by sintering at 1600°C for 2 h in air.

Keywords: Colloidal processing, Al₂O₃ foam, Particle-stabilized direct foaming, Porous ceramics

1. Introduction

Ceramic foams have a numerous applications such as catalytic reaction supports, filtration of hot gases, molten metal filters [1], supports for membranes, thermal insulators, bone grafting [2], and solid oxide fuel cell (SOFC) insulations [3]. There are a number of processing methods to manufacture the porous ceramics such as replica, sacrificial template but particle stabilized direct foaming is one of the promising routes in making porous ceramics with tailored microstructure [4]. Particle stabilized direct foaming technique has achieved a great attention because of its versatility and easy approach. Wet foams are thermodynamically unstable as they undergo coalescence, drainage and Ostwald ripening. In particle stabilized wet foams, partially hydrophobic particles goes on the air/water interface and makes an armor around the bubble to impede these destabilization mechanisms [5-11]. The energy for attaching particles is about 10³-10⁵ kTₛ, which tends the particles to adsorb irreversibly at the air/water interface. The adsorption of partially hydrophobic particles reduces the highly energetic interfacial area and lowers the overall free energy of the system [12]. The short chain amphiphiles such as valeric acid exhibit high solubility and high critical micelle concentration (CMC) in water [13], so its amount can be varied freely from 30 to 100 mmol/L. These valeric acid molecules tend to adsorb electrostatically with their hydrophilic head onto the particle surface leaving hydrophobic tail in contact with the aqueous medium [8]. In this article, we designed the microstructure of the porous Al₂O₃ by varying the amount of anionic surfactant (valeric acid), solid loading, and stirring speed followed by examining the microstructure, cell size distribution, and porosity.

2. Materials and Methods

High purity α-Al₂O₃ (AKP-30) used in this study was acquired from Sumitomo Chemicals Co. Ltd, Japan having particle size and BET surface area of 0.3–0.5 µm and...
5–10 m²/g, respectively. Valeric acid (C₅H₁₀O₂, 99% pure) was used as an amphiphile and purchased from Sigma-Aldrich. The colloidal system was made by using distilled water as a solvent and 2N HCl was added to maintain pH near 4.5. Different parameters such as variation in valeric acid, solid loading, and stirring speed were studied as shown in Table 1. The slurry was ball milled for 24 h with ball to powder ratio 2:1. After ball milling, the valeric acid was added and 1N NaOH solution was used to adjust final pH to 4.7, then foam making by using the stirrer with direct driven motor. The specimens were prepared by using perspex molds followed by drying for 24 h in humidity and temperature control chamber at 20°C with humidity of 90%. After 24 h, the temperature was increased to 30°C under same humidity conditions. After drying the specimens, sintering was carried out at 1600°C with heating rate of 1°C/min and dwell time was 2 h. A flow chart showing the detailed procedure in fabricating porous Al₂O₃ ceramic was shown in Fig. 1.

### 3. Results and Discussion

#### 3.1 Effect of valeric acid

In this article, we present the effect of variation in valeric acid on the microstructure of particle stabilized Al₂O₃ foam by fixing the solid loading at 35 vol.% and stirring speed at 1000 rpm. The isoelectric point (IEP) of Al₂O₃ was ~9, so the pH was kept at 4.7 in order to stabilize the colloidal system and to get the higher magnitude of zeta potential. Valeric acid was used as a short-chain amphiphile, which made the particles partially hydrophobic and decrease the surface tension due to enhanced adsorption of the partially hydrophobic particles at the air/water interface. Valeric acid has high critical micelle concentration (CMC) value, so it was varied from 30 to 100 mmol/L and effect on the microstructure was studied. At low valeric acid contents, the particles were not enough partially hydrophobic to stabilize the foam that resulted in large cell size due to coalescence and drainage but with increasing the valeric acid content, the stabilization of foam occurred that resulted in a small cell size with narrow distribution as shown in Fig. 2. The decrease in cell size of the foam occurred by increasing the valeric acid, because the foam viscosity increased with increasing amphiphile concentration in the initial suspension. Previous researchers [14] reported that, this increase in viscosity is due to the more pronounced screening of the particle surface charge achieved for higher concentrations of amphiphilic molecules adsorbed on the particle surface or free in the liquid medium. As a result of this screening effect, the thickness of the electrical double layer around the particles is reduced, decreasing the repulsive forces between them. The inter-particle attraction due to Van der Waals forces is thus favored due to screening effect, leading to an increase in foam viscosity.

### Table 1. Batches used in this study to manufacture the particle stabilized Al₂O₃ foam

<table>
<thead>
<tr>
<th>Batch</th>
<th>Valeric Acid (mmol/L)</th>
<th>Solid Loading (vol. %)</th>
<th>Stirring Speed (rpm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>30–100</td>
<td>35</td>
<td>1000</td>
</tr>
<tr>
<td>2</td>
<td>50</td>
<td>15–85</td>
<td>1000</td>
</tr>
<tr>
<td>3</td>
<td>50</td>
<td>45**</td>
<td>100–1000</td>
</tr>
</tbody>
</table>

*Shaded areas are variables in the experiments
**Stirring Speed experiments were done exceptionally at 45 vol.% solid loading, however our prior results showed that there was not much difference between 35 vol.% and 45 vol.% solid loading.

![Fig. 1. A flow chart showing the procedure in fabricating porous Al₂O₃ ceramic.](image)
Fig. 2. Effect of valeric acid on the cell size of Al₂O₃ foam (a) 30 mmol/L, (b) 50 mmol/L, (c) 70 mmol/L, and (d) 100 mmol/L.

Fig. 3. Effect of amount of valeric acid on (a) porosity, (b) average cell size, and (c) shrinkages of Al₂O₃ foam.
The surface tension of the colloidal system was decreased by increasing the amphiphile due to the presence of free amphiphilic molecules in the suspension [14]. By increasing the valeric acid above 80 mmol/L, again destabilization was observed and the cell size distribution became wider, which may be due to the fact that particles became more hydrophobic and unable to stabilize the foam bubbles. G. Kaptay determined that it is theoretically possible that if the contact angle of the particles is below 90° then a closely packed single layer of particles or loosely packed single layer of particles can be fabricated [11], so our foam strut wall was always a single layer as shown in insets of Fig. 2.

The effect of valeric acid on the porosity and average cell size was depicted in Fig. 3(a), and 3(b) respectively. The porosity of the Al₂O₃ foam can be varied by changing the amount of valeric acid and the plot between porosity and amount of valeric acid can be divided into three regions such as initial foam region, sound foaming region, and foam destabilization region. In the initial foam region, the wide cell size distribution was observed in the foam with average cell size between 80 to 186 µm, and porosity was more than 91%. In the sound foaming region, the foaming was very good with an average cell size of 65 µm and narrow distribution having the porosity between 88 to 90%. There was a sharp decrease in average cell size from 186 to 65 µm, when valeric acid was increased to 40 mmol/L, and that average cell size was almost constant up to 80 mmol/L, shown in Fig. 3(b). On further increasing the valeric acid above 80 mmol/L, again destabilization in foam occurred due to coalescence, Ostwald ripening, and drainage (foam destabilization region). Due to these destabilization mechanisms, the microstructure was not uniform having wide cell size distribution as already shown in Fig. 2(d). There was no significant change in linear shrinkages of the foam by varying the valeric acid concentration and found between 21 to 24% as shown in Fig. 3(c).

### 3.2 Effect of solid loading

The effect of solid loading on the microstructure of Al₂O₃ foam was studied by varying the Al₂O₃ content from 15 to 85 vol.%, whereas the valeric acid content and stirring speed was fixed at 50 mmol/L and 1000 rpm, respectively. Typical fractured surface of the Al₂O₃ foam consists of open and closed cells at the same time having wide cell size distribution. The effect of solid loading on the cell size of Al₂O₃ foam is shown in Fig. 4.

![Fig. 4. Effect of solid loading on the cell size of Al₂O₃ foam (a) 25 vol.%, (b) 45 vol.%, (c) 65 vol.%, and (d) 85 vol.%](image-url)
ing cell size ranged from 32 to 100 µm as shown in Fig. 4. At low solid loading, the large cell size of the foam with wide distribution was natural because less number of particles was present and viscosity of the colloidal suspension was low. By increasing the solid loading, the stabilization was improved due to more particles available to adsorb at the highly energetic air/water interface that resulted in smaller cell size with narrow cell distribution having single strut walls as shown in Fig. 4.

When the solid loading was increased from 15 vol.% to 25 vol.%, the wet foam volume increased twice, reaching the maximum point and again gradually start decreasing due to destabilizing mechanisms in the foam as shown in Fig. 5(a). By increasing the solid loading, there was a gradual decrease in average cell size from 100 to 32 µm due to strong increase in viscosity of the colloidal suspension that resulted in less air incorporation during foaming, and the porosity of foam was decreased from 93 to 75%, as shown in Fig. 5(b) and 5(c). There was a decrease in foam shrinkage from 30 to 20% by increasing the solid loading, and fixing the valeric acid content at 50 mmol/L, as depicted in Fig. 5(d). At low solid loading, the particles were not closely packed, which lead to more shrinkage during strut wall densification. Whereas at high solid loading, the particles were closely packed and less shrinkage occurred during the strut wall densification.

3.3 Effect of stirring speed

The bubble size of the foam was significantly influenced by the stirring speed which was varied from 100 to 1000 rpm by fixing solid loading at 45 vol.% and valeric acid at 50 mmol/L. It was found that there was no foam below stirring speed of 400 rpm. The foam was occurred at stirring speed of 400 rpm but with large bubble size, and by further increasing the stirring speed, the average bubble size was decreased. The sound foaming with small bubble size and narrow distribution was obtained with a stirring speed of 1000 rpm as shown in Fig. 6. The decrease in bubble size by increasing the stirring speed was mainly due to the shear stresses applied on the bubble surface during frothing, which caused the bubbles to rupture and divide into smaller bubbles and thus led to the foam with smaller average bubble size and narrow
bubble size distribution. The bubble rupture took place only if the shear stress applied overcomes the interfacial stress. The bubble size also depended on the viscosity of the suspension. As discussed in sections 3.1 and 3.2, the viscosity of the initial suspension was increased by increasing the amphiphile concentration and increasing the solid loading and it was observed that high viscosity of the initial suspension lead to the small bubble size and vice versa.

4. Conclusions

In this work, we showed that it was possible to tailor the finally sintered Al$_2$O$_3$ foam properties by varying the amount of valeric acid, solid loading and stirring speed. The microstructure, cell size, and porosity of the Al$_2$O$_3$ foam were designed successfully. The porosity can be varied from 75 to 93%, and cell size of the foam was between 20 to 300 µm. This showed that direct foaming technique was a versatile technique, and we could easily design the foam microstructure according to the application requirement.

Acknowledgements

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References


