I O U R N A L O F

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# Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> porous ceramics from particle-stabilized wet foam by direct foaming

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 $Al_2O_3$ -TiO<sub>2</sub> porous ceramics has been a focus of research due to its unique electric, thermal and mechanical properties. This study is a novel approach for the production of microporous ceramics consisting of  $Al_2O_3$  and TiO<sub>2</sub> fabricated by direct foaming. The colloidal  $Al_2O_3$  suspension was partially hydrophobized using propyl gallate as an amphiphile at pH 4.75. The different mole ratios of the TiO<sub>2</sub> suspension was added to the surface modified  $Al_2O_3$  suspension. The contact angle was found to be around  $60 \sim 65^\circ$  with the wet foam stability of about 90% at the mole ratio of 1 : 1. The free energy corresponds to 3.5  $\times 10^8$  kT including the Laplace pressure of about 2.2 mPa at the same mole ratio.

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

## Introduction

Porous ceramics with tailored porosity exhibit special properties and features that usually cannot be achieved by their conventional dense counterparts. Porous ceramics nowadays has many applications as end products and in several technological processes. In everyday life, macroporous materials are used in various forms and compositions, including for instance polymeric foams for packaging, aluminum light-weight structures in buildings and airplanes, high-temperature filters, thermal gas separation, and thermal structural materials [1, 2]. The addition of amphiphile molecules stabilizes the suspensions by making the suspended particles partially hydrophobic [3]. The modification of the chemical compositions of ceramic foams with a variety of functionalities is enabled by tailoring the contact angles of particles. The contact angle depends on surface chemistry, roughness, impurities, particle size, and surfactants etc. It can be determined by changing the surface chemistry of the particles or by adjusting the composition of the suspensions. Ceramic particles can achieve any contact angle (0 ° <  $\theta$  < 180 °) by adsorbing amphiphile molecules on their surfaces. The use of surfactant to determine the wetting ability of particles is a versatile approach for the surface modification of a wide range of ceramic and metallic materials [4].

The ceramic foams produced by direct foaming have

shown highest stability in some cases the wet state, and the mechanical properties can be increased with the increase in the additive concentration as well as increase in the sintering temperature. A three dimensional network is formed in the bulk-aqueous-phase, when the ability of the particles to form dense porous ceramics, around the bubble stabilizes the liquid films separating the bubbles. The attachment of the particles to the bubble-surface and a network or dense layer of particles at the liquid/ bubble interface, are responsible for foam stability [5].

However, the wet-foam bubbles in colloidal suspension are thermodynamically unstable systems due to the large area and high energy of their air/water interfaces. When particles are not completely wet in the liquid phase, colloidal particles attach to the gas/liquid interface. Here, the position of a particle at the interface is determined by a balance between the gas/liquid, gas/solid, and solid/ liquid interfaces, and particles so suspended are said to be partially hydrophobic [6].

 $Al_2O_3$  and  $TiO_2$  composite materials have a relatively moderate mechanical strength due to micro-cracks at the grain boundary induced by the high anisotropy of the thermal expansion coefficients [7]. Due to the brittle nature the porous ceramic components, it is avoided traditionally, unlike in metallic or polymeric products. Introduction of voids into the solid structures leads to the formation of porous ceramics using favorable conditions by direct foaming mechanism [8, 9].

In this work, we demonstrate the effect of  $TiO_2$  content in stabilizing colloidal suspensions to investigate the suitable wet foam stability as shown in Fig. 1. This process depends on various factors such as inter-particle

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**Fig. 1.** Schematic representation of the processing of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> porous ceramics by direct foaming.

interaction, surface tension, Laplace pressure, and adsorption free energy. The microstructure analysis done with the sintering of the dried samples to the porous ceramics.

### **Experimental Procedure**

#### Materials

The raw materials used in this study were high-purity alumina (Al<sub>2</sub>O<sub>3</sub>,  $d_{50} \sim 4 \mu m$ , Showa Chemicals Co. Ltd., Tokyo,Japan), rutile TiO<sub>2</sub> ( $d_{50} \sim 2.05 \mu m$ , Junsei Chemicals, Japan), de-ionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China).

#### Preparation of the colloidal suspensions

The initial suspension of Al<sub>2</sub>O<sub>3</sub> was prepared by ball milling 50 vol.% of alumina with 0.01 M NaOH and 0.01 M propyl gallate as an amphiphile. Homogenization and de-agglomeration were performed using zirconia balls (10 mm diameter with 2:1 ratio of balls to powder). Ball milling proceeded for 24 ~ 48 h and the solid concentration of the suspension was reduced to 30 vol.% in order to maintain the stability of the airflow by decreasing viscosity. The propyl gallate concentration of 2 wt.% was adjusted to the required concentration in the final Al<sub>2</sub>O<sub>3</sub> suspension. The pH of the suspensions were initially fixed at 4.75 exactly, according to the zeta potential of Al<sub>2</sub>O<sub>3</sub> adjusted by 0.1 M NaOH or 0.1 N HCl. Meanwhile, the TiO<sub>2</sub> suspension was ball milled proceeded for  $24 \sim 48$  h and the solid concentration of the suspension was reduced to from 50 vol.% to 15 vol.% initially. The TiO<sub>2</sub> suspension with increasing mole ratios was added to the ZrO<sub>2</sub> suspension and the mixture were stirred uniformly for  $10 \sim 15$  min. to produce Al<sub>2</sub>O<sub>3</sub>-AlTiO<sub>4</sub> wet foams of the final suspension with maximum stability under constant atmospheric conditions.

#### Contact angle and surface tension

The pendant-drop-method (KSV Instruments Ltd, Helsinki, Finland) and the sessile-drop-method was used to measure the surface tension and the contact angle of the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> suspension respectively. In the pendant-drop test, the force between the solid particles in the liquid phase, due to the surface tension, is proportional to the length of the boundary between the liquid and the tube, with the proportionality constant usually denoted by  $\gamma$ . Depending on the suspension contact angle and the surface tension, the drop volume varied between 5 and 10 µL.

#### Adsorption free energy, and laplace pressure

The foaming of 150 ml suspensions was accomplished using a household mixer (150 watt, Super Mix, France) at full power for 5 to 10 min. The bubble size-distribution of the foam was evaluated using an optical microscope in transmission mode (Somtech Vision, South Korea) with a connected digital camera, and measured using linear intercepts. The average- bubble-size was determined by analysis of 100 bubbles.

The outstanding stability of particle–stabilized interfaces is due to the high energy  $\Delta G$  required to remove an adsorbed particle of radius *r* from an interface of surface tension  $\Upsilon_{\alpha\beta}$ . This can be calculated using the following equation, where  $\theta$  is the contact angle formed between the particle and the interface [10].

$$\Delta G = \pi r^2 \Gamma_{\alpha\beta} (1 - \cos\theta)^2 for \ \theta < 90^{\circ} \tag{1}$$

According to Equation 1,  $\Delta G$  is greatest when  $\theta$  is 90°; however, foam stabilization of particles readily occurs when  $\theta$  is between 50° and 90°. Moreover, the stability of the thin liquid film between the air bubbles plays an important role in stabilizing wet foams, which decrease in thickness and eventually rupture due to foam drainage or to collision between bubbles [11].

Furthermore, due to the steady diffusion of gas molecules from smaller to larger bubbles over time, a broadening of the bubble size distribution occurs. The difference in the Laplace pressure between bubbles of distinct sizes (R) leads to bubble disproportionation and Ostwald ripening [12-14]. Due to the combined actions of these destabilization mechanisms, the liquid foam collapses. The pressure acting on gas bubbles in a colloidal suspension can be described by the Laplace pressure as:

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

where  $\Delta P =$  Laplace pressure (N/m<sup>2</sup>), is the pressure difference between the inner and outer surfaces of a bubble or droplet, the effect of which is caused by the surface tension  $\gamma$ (mN/m) at the interface between liquid and gas. R<sub>1</sub> and R<sub>2</sub>, radii of curvature for an

ellipse, are taken into consideration. However, for spherical bubbles,  $R_1$  and  $R_2$  are equal so we used the second formula for calculation of the Laplace pressure [15].

## Wet foam stability

The total porosity of sintered ceramics is proportional to the amount of bubbles incorporated into the suspension during the foaming process. Wet-foam stability can be defined by the reduction of the volume of the foams after they are dried at room temperature  $(20 \sim 25 \text{ °C})$ , and can be represented by the following equation.

Wet foam stability = 
$$\left(\frac{V_{\text{Final}}}{V_{\text{initial}}}\right) \times 100$$
 (3)

Where,  $V_{initial}$  is the volume of the initial wet foam prepared after the incorporation of air into the colloidal suspension and  $V_{final}$  is the volume of the final dried foam.

#### Drying and sintering

Wet samples were dried at  $20 \sim 25$  °C for  $24 \sim 48$  h. The dried foams were sintered in an electric muffle furnace at 1300 °C for 1 h. with the rate of heating and cooling 1 °C/min and 3 °C/min, respectively. The microstructures of the sintered foams were observed by using scanning electron microscopy (SEM, JEOL, Japan). The phase compositions of the samples were characterized by using X-ray diffractometry (XRD, Rigaku D/Max 2500, Japan).

## **Results and Discussion**

The contact angle of the suspension is an important parameter to determine the wetting ability of the particles in the colloidal suspension. As a result the hydrophobicity of the particles in the suspension can be controlled to a varied contact angle as shown in Fig. 2. The average contact angle of the  $Al_2O_3$ -TiO<sub>2</sub>



Fig. 2. Contact angle and surface tension of colloidal  $Al_2O_3$ -Ti $O_2$  suspension with respect to mole ratio of Ti $O_2$ .



**Fig. 3.** Adsorption free energy vs. wet foam stability with respect to the mole ratio of  $TiO_2$ .



Fig. 4. Average bubble size vs. average pore size with respect to the mole ratio of  $TiO_2$  colloidal suspension.

suspension is decreased initially with the increase in mole ratio of 1:0.25 to 1:0.5. But with the further increase in the content of TiO<sub>2</sub> the average value of the contact angle increases, which is due to the increase in the viscosity of the suspension. With the corresponding increase in the viscosity of the suspension with the mole ratio of TiO<sub>2</sub> the surface tension is decreased from 165 mN/m to 90 mN/m.

Fig. 3 shows the change in adsorption free energy with the different mole ratio of TiO<sub>2</sub>. The propyl gallate (2 wt.%) solution used to hydrophobize the Al<sub>2</sub>O<sub>3</sub> suspensions. It shows the adsorption free energy (calculated using Eq. 1) was found to increase with the increase in the mole ratio. The adsorption free energy is directly related to the contact angle of the suspension. Hence, with the gradual increase in the contact angle (as per Fig. 2) the adsorption free energy is increased gradually from  $7.0 \times 10^7 \text{ kT}$  to  $4.1 \times 10^8$ kT with the increase in the mole ratio of TiO<sub>2</sub> till 1:1.5. Due to the consequent increase in the TiO<sub>2</sub> content, the suspension gets to be viscous which leads to a gradual increase in the surface tension, including the wet foam stability. The highest wet foam stability of around 90% was found to be at the mole ratio of



**Fig. 5.** Laplace pressure vs. wet foam stability with respect to the mole ratio of TiO2 colloidal suspension.

1:1. Hence we can consider that that with the high increase in adsorption free energy the wet foam stability was found to increase gradually.

After foaming of the colloidal suspension the bubble size can be determined using an optical microscope. In Fig. 4 the average bubble size vs. the average pore size of the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> suspension was plotted with respect to the different mole ratio of TiO<sub>2</sub>. The average bubble size of the colloidal suspension is decreased from 140  $\sim 88 \,\mu\text{m}$ . Similarly, the pore size decreases gradually with the increase in the content of TiO<sub>2</sub>. This shows that though wet foam stability is the highest with the mole ratio of 1:1 but the average bubble size as well as the average pore size is lowest at that mole ratio. Hence, it can be proved that with the lowering of the bubble size increases the stability of the wet foam in the colloidal suspension.

Fig. 5 shows the wet foam stability corresponding to the Laplace pressure exerted by the bubbles of the wet foams produced with respect to the different mole ratio of TiO<sub>2</sub>. This can be calculated using Eq. 2, using the surface tension and the average bubble size of the colloidal suspension and the wet foam respectively. The Laplace pressure of the wet foams is found to increase with the increase in the mole ratio of TiO<sub>2</sub>. It was found to be highest at 1:0.75 of around 2.8 mPa, which gradually decreases with the increase in the TiO<sub>2</sub> content. This can be explained from Eq. 2 as well, where the average bubble size is inversely proportional to the Laplace pressure, so the correspondence lies to Fig. 4. Moreover, the wet foam stability of the Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> suspension was increased with the increase in the mole ratio of TiO<sub>2</sub> and was found to be highest of around 90% at 1 : 1 mole ratio of  $TiO_2$ 

The XRD analysis on the crystalline phase are presented in Fig. 6 which  $Al_2O_3$ ,  $Al_2TiO_5$  and  $TiO_2$  in sintered  $Al_2O_3$ -TiO<sub>2</sub> ceramics with respect to different mol% of  $Al_2O_3$ -TiO<sub>2</sub> colloidal suspension. The main intensity peak of the different composites were identified with peak at 25.5 degrees (hkl = 012) for the



**Fig. 6.** XRD patterns for  $Al_2O_3$ -TiO<sub>2</sub> sintered porous ceramics: (a) 1 : 0, (b) 1 : 0.25, (c) 1 : 0.5, (d) 1 : 0.75, (e) 1 : 1, and (f) 1 : 1.5 sintered at 1300 °C for 1 h.



**Fig. 7.** Microstructures of porous ceramics of  $30 \text{ vol.}\% \text{ Al}_2\text{O}_3$  with respect to different mole ratios of TiO<sub>2</sub>: (a) 1 : 0, (b) 1 : 0.25, (c) 1 : 0.75, and (d) 1 : 1, sintered at 1300 °C for 1 h.

corundum phase, at 26.5 degrees (hkl = 101) for  $Al_2TiO_5$  phase and at 27.5 degrees (hkl = 110) for the rutile phase, respectively. The Al<sub>2</sub>TiO<sub>5</sub> peaks show already higher intensity compared to the other components which shows the greater impact of the reaction at the low temperature of 1300 °C in the sample, which concurs with the observed for pure Al<sub>2</sub>TiO<sub>5</sub> (rate constant/k =  $1.3 \times 10^{-19} \text{ m}^2/\text{s}$  [16]. The trace of rutile  $TiO_2$  (hkl = 110) at 26.5 degree can be attributed to the low temperature to the formation of Al<sub>2</sub>TiO<sub>5</sub> phase in the sintered sample. The amount of unreacted Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> kept on decreasing. This proves that at the low sintering temperature with higher mole ratios of Al<sub>2</sub>O<sub>3</sub>-TiO<sub>2</sub> the complete transformation of Al<sub>2</sub>TiO<sub>5</sub> can occur, which as a result might lead to the good thermal shock resistance of the sintered porous ceramics [7].

The microstructure of  $Al_2O_3$  porous ceramics with the addition of different mole ratios of TiO<sub>2</sub> are shown in Fig. 7. Open pores exhibiting interconnecting windows (Fig. 7(a)) are obtained if particles isolate at the plateau borders of the foam due to bubble disproportionation [9]. On the other hand, closed pore are typically achieved when the particles are distributed around the air bubbles upon setting as shown in Fig. 7(b). Fig. 7 (c) and (d) show uniform and narrow size distribution of pore size in the range of 70 to 24  $\mu$ m. With the consequent increase in the TiO<sub>2</sub> content in porous ceramics of different mole ratio of TiO<sub>2</sub> decreases the pore size from 100 to 20  $\mu$ m. The inset pictures of each mole ratio shows the higher magnifications of the same microstructures where the increase in the finer pore densification can be seen.

#### Conclusions

The addition of TiO<sub>2</sub> to the Al<sub>2</sub>O<sub>3</sub> suspension increased the wet-foam stability of the suspension. Particles stabilize wet foams by causing steric hindrance to the coalescence of bubbles, and by modifying the colloidal properties of the interfaces. The interface-contact angle stability of ceramic foam is directly related to the surface energy of the colloidal suspension which corresponds to the calculation of free energy and Laplace pressure of the ceramics. From the above experiment we conclude that a stabilizing point was obtained for the production of porous ceramics was in the mole ratio of 1:1. The adsorption free energy and the Laplace pressure of the porous ceramic materials corresponds to  $3.5 \times 10^8 \text{ kT}$ and 2.2 mPa at a mole ratio of  $Al_2O_3$  to  $TiO_2$  of 1 : 1. The highest wet foam stability was found to be around 90% with a contact angle of about  $60 \sim 65^{\circ}$ . The microstructure analysis shows the reduction in the pore size with the increase in the TiO<sub>2</sub> content in the colloidal suspension.

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