ZrO₂–TiO₂ porous ceramics from particle stabilized wet foam by colloidal processing

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ZrO₂–TiO₂ porous ceramics recently has been great interest in the dielectric resonator materials, as well as in the fields of preparation of optical devices, and bio materials. This study reveals an approach for the production of micro porous ceramics consisting of TiO₂ and ZrO₂ fabricated by colloidal wet processing. ZrO₂ particles in the colloidal suspension was partially hydrophobized using propyl gallate as an amphiphile, with a suitable pH range. The different mole ratios of the TiO₂ suspension was added to the surface modified ZrO₂ suspension. The contact angle was found to be around 75° with the adsorption free energy of 1.8×10^{-11} – 2.15×10^{-11} J. The Laplace pressure of about 1.48–1.24 mPa was determined corresponding to the wet foam stability of about 76–80%. The microstructure analysis is done after sintering the dried samples for obtaining the porous ceramics.

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1. Introduction

Porous ceramic materials nowadays are used in numerous fields such as filtration of molten metals or hot gases, photo catalysis for solar energy conversion, environmental applications for water and air purification, refractory insulation of furnaces, separation, humidity sensors, acoustic absorbers, refractory and insulation furnaces as well as biomaterials for hard tissue repair engineering.^{1)–3)} The dielectric resonators made from tin modified ZrTiO₄ for satellite telecommunication ranging from cellular telephones to global positioning systems has been a focus of great interest.⁴⁾

Solid state reactions has been used in the preparation of ZrTiO₄ based ceramics traditionally, with ZrO₂ and TiO₂ powders at high temperatures (above 1400°C). The functional properties of the ceramic material, treatments consuming a high amount of energy after the reaction are generally necessary and expensive.⁵⁾ Controlling the morphological properties of materials during synthesis is of great importance, as these structural characteristics strongly influences their performances and purposes.⁶⁾

Porous ceramics can be fabricated by a variety of methods including, the replica technique, the sacrificial template method, and the direct foaming technique.⁷⁾ To control these features and allow formation of either open or closed cell ceramics with remarkable stability, direct foaming technique is used.⁸⁾ The processing route determines the microstructure of the final macro-porous ceramic. Therefore, the selection of a given processing method depends strongly on the microstructures needed in the end application.⁹⁾

The direct foaming technique is suitable for the preparing open and closed porous structures with varied porosities. Here we used this technique due to its inherent features such as versatility,

simplicity, and cost. In this method the air is directly incorporated into the suspension or liquid media, which is subsequently set in order to keep the structure of air bubbles created.¹⁰⁾ The incorporation of the gaseous phase is carried out either by mechanical frothing, injection of a gas stream, gas-releasing chemical reactions, or solvent evaporation.

In general, wet foams are thermodynamically unstable because of their large air-water interfacial area and thus high adsorption free energy. Surfactants are used to reduce the free energy of wet foams by lowering the air-water interface tension.¹¹⁾ The long or short chain surfactants used can reduce the surface tension, increase the surface viscosity and create electrostatic forces to prevent foam from collapsing.¹²⁾ Irreversible destabilization mechanisms of colloidal suspensions include drainage, coalescence, and Ostwald ripening. When particles are not completely wet in the liquid phase, colloidal particles attach to the gas/liquid, gas/solid, and solid/liquid interfaces, and particles so suspended are said to be partially hydrophobic. To improve the stability of wet foams particles have been used to adsorb at the air-water interface. The adsorption of particles reduces the highly energetic interfacial area and lowers the free energy of the system.¹³⁾

The aim of this work is to investigate the stabilization of foams with colloidal particles and the development of a processing route for the fabrication of solid macro porous ceramics with controlled microstructure. The effect of TiO₂ as an additive has been demonstrated in the experiments carried out at a suitable pH range. The addition of TiO₂ to the surface modified ZrO₂ increases the wet foam stability, which is causes steric hindrance to the coalescence of bubbles, and also modifies the colloidal properties of the interfaces, with the possible reaction as mentioned below:

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2. Experimental procedure

2.1 Raw materials

The experiments were carried out using high-purity ZrO₂ (baddeleyite polymorph, d₅₀ ~14.77 μm, >99.0% purity, density ~5.68 g/cm³, Showa Chemicals Co. Ltd., Japan), TiO₂ (rutile polymorph, d₅₀ ~2.05 μm, >99.0% purity, density ~4.23 g/cm³, Junsei Chemicals, Japan), and Poly ethylene glycol (Sigma-aldrich, Germany). Other chemicals used in the experiments were de-ionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China).

2.2 Preparation of colloidal suspensions

The suspension was prepared by adding 50 vol.% of ZrO₂ powder to an aqueous mixture of 1–2 ml of 0.01 (M) of propyl gallate as an amphiphile and 1–2 ml of 1 (N) NaOH. Homogenization and de-agglomeration were performed using zirconia balls (10 mm diameter with 2:1 ratio of balls to powder). The solid loadings and pH of the suspensions were initially fixed continuing the ball milling procedure for 24–48 h. The solid concentration of the ZrO₂ 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 ZrO₂ suspension. The propyl gallate (2 wt% to ZrO₂) was added to the ZrO₂ suspension for the partial hydrophobization of the particles at a pH range of about 3.5–4.5. Meanwhile, the aqueous TiO₂ solution was ball milled proceeded for 24–48 h and the solid concentration of the suspension was reduced from 50 to 15 vol.% initially. The TiO₂ suspension with different mole ratios was added to the ZrO₂ suspension and the mixture were stirred uniformly for 10–15 min. Finally 2 wt% of poly ethylene glycol was added to the final ZrTiO₄ suspension under constant atmospheric conditions.

2.3 Contact angle, surface tension and adsorption free energy

The pendant-drop-method (KSV Instruments Ltd., Helsinki, Finland) was used to measure the surface tension of the ZrTiO₄ suspension, whereas the sessile-drop-method was used to measure the contact angle of the same. In the pendant-drop test, a drop of liquid is suspended from the end of a tube by surface tension. 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 γ . Depending on the suspension contact angle and the surface tension, the drop volume varied between 5 and 10 μl.

The variation in the stability of wet foam at the particle-stabilized interfaces is due to the adsorption free energy (ΔG) required to remove an adsorbed particle of radius r from an interface of surface tension $\gamma\alpha\beta$. This can be calculated using Eq. (1), where θ is the contact angle (°) formed between the particle and the interface.¹⁴⁾

$$\Delta G = \pi r^2 \gamma_{\alpha\beta} (1 - \cos\theta)^2 \text{ for } \theta \leq 90^\circ \quad (2)$$

According to the above equation, ΔG (J) is greatest when θ is 90°; however, foam stabilization of particles readily occurs when θ 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.

Fig. 1. Estimation of Laplace pressure and adsorption free energy from the partially hydrophobized colloidal suspension.

2.4 Foaming, air content and Laplace pressure

The foaming of 100 ml of each suspension was accomplished using a household hand mixer (150 W, Super Mix, France) at full power for 15 to 20 min. The partial hydrophobization of the particles can be seen in Fig. 1. 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 the software Linear Intercept (TU Darmstadt, Germany). The average bubble size was determined by the analysis of 100 bubbles in a composition.

The volume of air or voids in suspension in aggregate particles is called the air content (%) of the suspension, and is usually expressed as an increased percentage of total volume of air in the mixture before and after foaming. The air content of an initial colloidal suspension measures the instance of the wet foam stability of a suspension. It can be measured by the following equation:

$$\text{Air Content (\%)} = \frac{(V_{\text{wet foam}} - V_{\text{suspension}})}{V_{\text{wet foam}}} \times 100 \quad (3)$$

Where, $V_{\text{wet foam}}$ indicates the wet foam volume after foaming and $V_{\text{suspension}}$ indicates volume of suspension before foaming.⁸⁾

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. 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:

$$\Delta P = \gamma \left(\frac{1}{R_1} + \frac{1}{R_2} \right) = \frac{2\gamma}{R} \text{ (For spherical bubble)} \quad (4)$$

where ΔP = Laplace pressure (mPa), is the pressure difference between the inner and outer surfaces of a bubble or droplet, this effect is caused by the surface tension γ (mN/m) at the interface between liquid and gas. R_1 and R_2 , 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⁾

2.5 Drying and sintering

Wet samples were dried at 50°C for 24–48 h in a sterilizer. The dried foams were sintered in a super kantel furnace (max. 1650°C) at 1600°C for 1 h with the rate of heating and cooling

1 and 3°C/min, respectively. The microstructures of the sintered foams were observed by field emission scanning electron microscopy (FESEM, JEOL, Japan). The phase compositions of the samples were characterized by X-ray diffractometry (XRD, Rigaku D/Max 2500, Japan).

2.6 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 (20–25°C), and can be represented by Eq. (4).¹²⁾

$$\text{Wet foam stability (\%)} = \left(\frac{V_{\text{final}}}{V_{\text{initial}}} \right) \times 100 \quad (5)$$

3. Results and discussion

The contact angle of the colloidal particles at fluid interfaces depends on the surface chemistry, roughness, impurities, particle size, as well as on the composition of the fluid phases. The carbon and polymeric materials exhibit low surface free energy and thus are not easily wetted by apolar and polar liquids. This leads to high contact angle ranges at the gas-water-solid interfaces. Contrary to the metallic and ceramic materials exhibit very high surface free energies and therefore are fully wettable by any apolar or polar liquid.¹⁶⁾ The degree of particle hydrophobization achieved through the surface adsorption of amphiphiles was investigated with the help of surface tension measurements. A decrease in the surface tension upon increasing the initial additive concentration is observed for the evaluated suspensions.¹⁰⁾

Contact angle of the particles at the interface determines the wetting ability, by the extent to which they are hydrophobic as shown in Fig. 2. The average contact angle of the colloidal suspension increased from 71–75° with the increase in the mole ratio of TiO₂ to 1:1.25. But a lower range of contact angle has been observed with the further increase in the TiO₂ content. This is due to the increase in the viscosity of the particles in the colloidal suspension. Moreover, the surface tension of the suspension (the contractive tendency of the outer surface of the liquid) decreases at the same mole ratio of about 1:1.25 to about 65 mN/m where the wet foams were found to be the most stable. Further with the increase in the TiO₂ content they were observed to gradually decrease which leads to lower wet foam stability.

Fig. 2. Contact angle and surface tension of colloidal suspension with respect to mole ratio of TiO₂.

The adsorption free energy of surfactant adsorption is a surface excess of the Gibbs thermodynamic potential and is widely used as a basic thermodynamic characteristic of surfactants.¹⁷⁾

Figure 3 shows the change in adsorption free energy in relation to the wet foam stability, with respect to the TiO₂ content where propyl gallate (2 wt%) was used to stabilize the ZrO₂ initial suspensions. It interprets an increase in the free energy (1.8×10^{-11} – 2.15×10^{-11} J) as well as the wet foam stability till around 80% with the increase in the mole ratio till 1:1.25, as per Eq. (2) with the increase in the contact angle (where the radius of the TiO₂ particle is calculated, the contact angle and surface tension were measured by the sessile-drop method and the pendant-drop method, respectively). With the further increase in the TiO₂ content the free energy were found to decrease gradually with minimum value of about 5.1×10^{-12} J corresponding to lower the wet foam stability. Henceforth, it can be proved that 1:1.25 is the most stable zone for the wet foams in our experiment.

The air content, calculated as per Eq. (3), of an initial colloidal suspension measures the instance of the wet foam stability of a suspension. In Fig. 4, the air content of the suspension increases initially with the increase in the TiO₂ content till 1:1.25 of about 67%. The wet foam stability has been found to be the highest at that mole ratio. Moreover, with the increase in the TiO₂ content both the air content and the wet foam stability were found to be reduced. This is due to the increase in the particle concentration of the colloidal suspension it tends to become more viscous

Fig. 3. Adsorption free energy vs. wet foam stability with respect to the mole ratio of TiO₂ in the colloidal suspension.

Fig. 4. Air Content vs. wet foam stability with respect to the mole ratio of TiO₂ in the colloidal suspension.

Fig. 5. Laplace pressure vs. wet foam stability with respect to the mole ratio of TiO_2 in the colloidal suspension.

Fig. 6. Average bubble size vs. average pore size with respect to the mole ratio of TiO_2 in the colloidal suspension.

which in result reduces the air intake as well as the wet foam stability of the foam.

Figure 5 shows the wet foam stability corresponding to the Laplace pressure exerted by the bubbles of the wet-foams formed with respect to the particle concentration. This can be calculated using Eq. (4) (where the surface tension is measured by the pendant-drop method, and the radii of the larger and smaller bubbles are measured by optical microscopy). The difference in pressure decreased initially, as the bubble size increased (as shown in **Fig. 6**), and the stability also increased until the TiO_2 concentration of 1.25 (mole ratio), which corresponded to the particle concentration. The wet foam stability of around 80% at pressure range of about 1.48–1.24 mPa, which correspond to TiO_2 content of 1:1.25 mole ratio. Further increase in the solid loading resulted in a variable pressure, as well as corresponding wet-foam stability, because they are inversely related with the average bubble size of the wet foams.

In **Fig. 6**, the bubble size increased gradually from 82–98 μm with increasing mole ratio of TiO_2 in the colloidal suspension from 1:1 to 1:1.25. The bubble size increases gradually with further increase in the mole ratio of TiO_2 till 1:1.50. Similarly, the pore size decreased gradually with increasing TiO_2 content, which gradually increases with further increases in content TiO_2 in the colloidal suspension. This proves the effect of Laplace pressure (as shown in **Fig. 5**) which is inversely related to the

Fig. 7. Relative average bubble size of the ZrTiO_4 ceramic wet foams with respect to the time after direct foaming.

Fig. 8. XRD patterns for ZrO_2 - ZrTiO_4 sintered porous ceramics: (a) 1:1, (b) 1:1.25, (c) 1:1.50, (d) 1:1.75, and (e) 1:2, sintered at 1600°C for 1 hr.

average bubble size. The bubble size and pore sizes of the wet and dry foams were found to be 98 and 88 μm at the mole ratio of 1:1.50 of ZrO_2 to TiO_2 with the highest wet foam stability.

Figure 7 shows the relative bubble size with respect to time where after 1 hr the bubbles tend to collapse due to Ostwald ripening with a gradual increase in the bubble size. At the mole ratio of 1:1.25 of ZrO_2 to TiO_2 has the maximum relative increase in bubble size. The bubbles with the mole ratios of 1:1.5 and 1:1.75 are found to be the most stable due to high wet foam stability, whereas the mole ratios of 1:1 are found to be considerable with drastic increase in the relative bubble size with respect to time because of the excess of TiO_2 particles in the ceramic suspension respectively. Hence, from the above figure we can imply that the TiO_2 content is an important parameter for the stability of the wet foams.

In **Fig. 8** the XRD analysis on the crystalline phase, the patterns point to a high crystallinity of all ZrTiO_4 porous ceramics can be seen. The observed Bragg peaks are undoubtedly identified as ZrTiO_4 for the samples of different mole ratio of the ZrO_2 - TiO_2 suspension. The main intensity peak of the different composites were identified with peak at 27 degrees ($hkl = 110$) for the rutile TiO_2 phase, at 28 degrees ($hkl = 111$) for the baddeleyite ZrO_2 phase, and at 30 degrees ($hkl = 111$) for the

Fig. 9. Microstructure of porous ceramics of 30 vol.% ZrO₂ with respect to the different mole ratio of TiO₂: (a) 1:1.25, (b) 1:1.50 (c) 1:1.75 and (d) 1:2, sintered at 1600°C.

ZrTiO₄ phase. ZrTiO₄ phase shows higher intensity compared to the other components which shows greater impact of the reaction at the temperature of 1600°C. The amount of unreacted ZrO₂ and TiO₂ kept on decreasing. This proves with higher mole ratios of ZrO₂-TiO₂ the complete transformation of ZrTiO₄ can occur, which as a result might lead to the good mechanical and thermal properties of the sintered porous ceramics.¹⁸⁾

In Fig. 9, the microstructure exhibits variable patterns of the distributions of larger and smaller open pores. The porous ceramics in Figs. 9(a) and 9(b) shows the enlarged view of the greater sized pores. The rough and uneven distribution of pores along the surface of the sintered ceramics can be seen. The magnified views in Figs. 9(c) and 9(d) shows a hierarchical pore-distribution from larger to smaller pores. The corresponding decrease in the pore size of the sintered ceramics with the bubble size of the wet foam (comparing with Fig. 6) interprets lowers the chance of destabilization mechanisms.

4. Conclusions

The calculation of the free energy and Laplace pressure for a corresponding interface-contact angle stability of ceramic foam is directly related to the surface energy of the colloidal suspension. From the above experiment we conclude that a stabilizing point was obtained for the production of porous ceramics was in the mole ratio of 1:1.25. This stabilization point can be considered by adjusting the solid content of the suspension, which is directly related to the free energy of about 1.8×10^{-11} – 2.15×10^{-11} J

and the Laplace pressure in the range of 1.48–1.24 mPa, and which corresponds to the wet-foam stability of sintered porous ceramics. Wet-foam stability of around than 83% was established, at the mole ratio of 1:1.25 which can be considered as the most stable zone corresponding to the fine porous microstructures. The XRD patterns shows the increase in the ZrTiO₄ content with the increase in the mole ratio of the TiO₂.

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