

Stabilization of Wet Foams for Porous Ceramics Using Amphiphilic Particles

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ABSTRACT

Wet foams formed through direct foaming were stabilized using various concentrations of amphiphilic particles that could control pore size and porosity. These porous materials showed moderate strength upon compression with high porosity. Bubble size and wet foam stability were tailored by amphiphile concentration, particle concentration, contact angle, and pH of the suspension to obtain crack-free porous solid after sintering. Closed and open pores were obtained with sizes of 30~300 μm and porosities of over 80%.

Keywords: Contact angle, Amphiphile concentration, Wet foams, Bubble size

1. Introduction

Porous ceramics are of interest due to their potential applicability in catalysis, adsorption and separation, filtration of molten metals or hot gases, refractory insulation of furnaces, and hard tissues repair and engineering.^{1,2)} Ceramic foams produced by direct foaming have shown unprecedented stability in the wet state and elevated mechanical properties when sintered.^{3,4)} These wet foams were stable over several days and showed no bubble coarsening, drainage, or creaming. Their stability was attributable to the irreversible adsorption at the air-water interface of colloidal particles that were rendered partially hydrophobic by short-chain amphiphiles. The amphiphiles modified *in situ* the wetting behavior of the particles' surfaces.^{5,6)} Control of particle wetting allows the preparation of suspensions containing high concentrations of such partially hydrophobic particles. Suspensions could be foamed homogeneously throughout their entire volume, with porous bulk materials obtained upon drying and sintering. Such materials comprise mostly closed-porous microstructures with enhanced mechanical properties.^{7,8)}

Direct foaming is of particular interest due to its simplicity, low cost, and versatility. However, interconnected pore structures and the ability to solidify without sintering are often required. This work reports the effects of different processing parameters on the final microstructures of porous ceramic foams. This should aid the development of tailored foam microstructures and the production of open or closed porous foams with variable and controlled pore morphologies and porosities.⁹⁾ In this work, the stabilization of wet foams with colloidal parti-

cles and the influences of the particles' concentration and the effects of amphiphiles in the suspensions were assessed. Contact angle, pH, composition of the initial suspension and their effects on the wet foams' stability and bubble size were tested.

2. Experimental Procedure

2.1. Materials

High-purity alumina was from Showa Chemical, Tokyo, Japan and silica was from Junsei Chemical, Japan. Deionized water, hydrochloric acid (35% Yakuri Pure Chemicals, Osaka, Japan), sodium hydroxide powder (Yakuri Pure Chemicals, Kyoto, Japan) and propyl gallate (Fluka, China) were also used.

2.2. Suspension preparation

Suspensions were prepared using propyl gallate as an amphiphile by the stepwise addition of alumina powder to an aqueous mixture of 0.01 M NaOH and 0.1 M propyl gallate. Suspensions' solid loadings and pH were initially fixed as 50 vol% and 9.9 respectively. Homogenization and de-agglomeration were carried out by ball milling for at least 24 hours using polyethylene milling pots and alumina balls (10 mm in diameter, 2 : 1 ratio of balls to powder). The propyl gallate was adjusted to the required concentration in the final suspension (1~2 wt%). It was dissolved in NaOH (pH > 10) and added dropwise to the ball milled suspension under slight stirring to avoid local particle agglomeration. Finally, pH was set to 9.9 and water was added until the solid contents were 30 vol%. In other experiments, various pH suspensions were tested.

The SiO₂ suspensions were prepared by adding dry silica powder to water to achieve solid loadings of 50 vol%. The silica was unmodified and no further pH modification was required. The suspensions were then de-agglomerated and homogenized by alumina ball milling. The silica was then added drop wise

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added under stirring to the alumina suspensions containing propyl gallate. The pH was set as 9.9; it was varied in other tests. The mixtures' total solid contents were fixed as 30 vol%. Various blends of modified and unmodified particles were prepared and tested with total solid contents of 30 vol% under varying pH conditions.

2.3. Contact angle and surface tension

The suspensions' contact angles and surface tensions were measured by the pendant drop method (KSV Instruments Ltd, Helsinki, Finland). Al_2O_3 suspensions were prepared by the dropwise addition of propyl gallate to give solid loadings of 30 vol% alumina. Drop volume was varied between 5 and 10 μl depending on the suspension's contact angle and surface tension.

2.4. Foaming, drying, and sintering

Foaming of 150 ml suspensions was carried out using a household mixer (Super Mix, France, 150 watt) at full power for 3~5 min. Foams' bubble size distributions were evaluated by optical microscopy in transmission mode (Somtech Vision, South Korea) with a connected digital camera. Bubbles' sizes were measured using linear intercepts. Their average sizes were determined from the analyses of particular areas. Wet samples were shaped into cylinders by hand and subsequently dried in air at 20~25°C for 24~48 h. The dried foams were sintered in an electric furnace (Muffle Furnace) at 1200°C for 2 h. Heating was at 1°C/min and cooling was at 3°C/min.

3. Results and Discussion

3.1. Initial particle concentration

The microstructures of wet foams can be tailored by the concentration of particles in the suspension. The influence of particle concentration on the microstructure of wet foams was determined by varying the solids content in an alumina suspension containing particles at pH 4 and a propyl gallate concentration of 0.1 wt% in a suspension containing 50 vol% alumina. Average bubble size decreased greatly from 300 to 50 μm with increasing solid content from 10 to 50 vol% alumina (Fig. 1). The foams' air contents decreased from 82 vol% to 60 vol% over this range of solid concentrations. The decrease of air contents with solids contents over 50 vol% greatly increased the initial suspensions' viscosities. The minimum particle concentration required for the formation of stable foams was 10 vol% in this case. The size distribution of bubbles in the foams was wide at low solid contents and narrower at higher particle concentrations.⁴ The mixture of modified and unmodified particles showed similar properties with increasing particle concentration, with the only exception being the destabilization of suspensions with high silica contents. Ratios of alumina to silica of 0.1~0.3 resulted in stable foams with high porosity.

3.2. Initial amphiphile concentration

The amphiphile concentration of the initial suspension

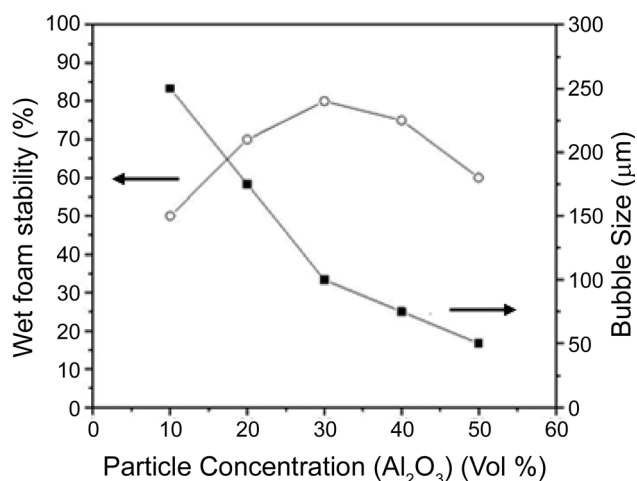


Fig. 1. Wet foam stability and bubble size with respect to alumina concentration in the initial suspension.

directly affects the colloidal particles' hydrophobicity; varying the particle concentration with constant amphiphile addition also affects particles' hydrophobicity. Increasing the initial amphiphile concentration increased adsorption onto the particles, enhancing their surface hydrophobicity.^{5,6} Above a critical concentration of adsorbed amphiphiles, particles became sufficiently hydrophobic to adsorb to the air-water interfaces, stabilizing freshly introduced air bubbles. Therefore, foam formation and the resulting microstructures depended strongly on the suspensions' initial amphiphile concentrations. Additional increases of amphiphile concentration greatly increased the suspension's viscosity, hindering the incorporation of air for foam formation.⁷ The concentration of amphiphile also affected the suspensions' contact angles and surface tensions, which directly influenced wet foam stability and bubble size and distribution. The effects of amphiphile strength on bubble size and wet foam stability were assessed and are discussed below (Fig. 2). Despite the wet foams having nearly similar 75 vol% air contents, their average bubble sizes decreased from c.a. 150~30 μm as propyl gallate concentration increased from 0.001 M to 1 M. Foams with lower average bubble sizes also exhibited narrower bubble size distributions.

3.3. Suspension pH

The effects of particle concentration on microstructure were determined by testing solid contents in up to 50 vol% alumina suspensions at pH 4~10 with a propyl gallate concentration of 0.1 wt%. Besides the concentration of amphiphile, the suspension's pH also affected the wet foam microstructure. Suspension pH affected air contents, average bubble sizes, and bubble size distributions of wet foams prepared from suspensions containing 30 vol% mixed alumina and silica particles and a constant amount of propyl gallate (Fig. 3). Highly aerated foams with small, narrowly distributed bubbles were achieved at pH (4~6). Higher pH (8~10) resulted in foams with larger bubble and wider distributions.

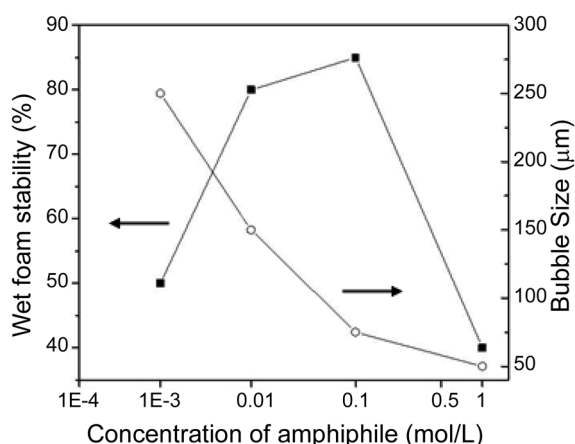


Fig. 2. Wet foam stability and bubble size with respect to amphiphile concentration in the initial suspension.

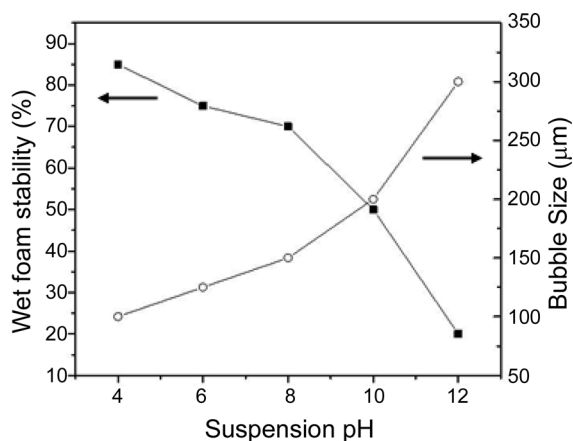


Fig. 3. Wet foam stability and bubble size with respect to suspension pH before foaming.

3.4. Contact Angle

Adsorption at fluid interfaces occurs when particles are not completely wetted and exhibit finite equilibrium contact angles at the triple phase boundary. The equilibrium contact angle (θ) results from the balancing of all the interfacial tensions. Oil (air)-in-water emulsions and foams result from contact angles below 90° and water-in-oil (air) emulsions and mists result from contact angles of 90° to 180° .⁶⁾ Once the contact angle of particles has been tuned, emulsions and foams can be prepared by (a) mechanical shearing, (b) injection, or (c) internal phase transformations and chemical reactions that lead to aeration or emulsification. Stable bubbles require particles that are strongly adsorbed at the interface and that impede destabilization mechanisms such as coalescence and Ostwald ripening. Stabilization has been reported to be achieved at intermediate contact angles of 40° ~ 86° in oil (air)-in-water emulsions and foams. This is corroborated by this work's results.⁷⁾ Controlling the contact angle of particles at the interface is of major importance when applying the processing routes outlined, since it determines the percentage of wet foam stability and bubble size. (Inset Fig. 4)

3.5. Microstructures of wet and sintered foams

The high stability of the wet foams allowed their direct drying in air at room temperature. However, to avoid cracking, the wet foams had to be slightly strengthened to overcome capillary stresses and to avoid differential shrinkage within the drying foam. Cracking was avoided by coagulating the particles by the internal pH-shift reactions.⁸⁾ The resulting macroporous structures exhibited a total porosity of 82%. Cells were mostly closed with an average size of c.a 50~150 μm . Single cells were separated by walls with minimum thicknesses below 1 μm . The foam cells were predominantly closed due to the air bubbles of the original wet foams being completely or partially covered with the surface modified particles. The subsequent drying and sintering then resulted in closed cells. Compared with surfactant-stabilized foams, these foams achieved smaller average cell sizes and exhibited either open or closed cells, even at high porosities. The smaller cells resulted from the high stabilities of the wet foams, which impeded bubble coarsening. Fig. 5(a, b) shows the bubble size and distribution of the wet foams in acidic and basic conditions

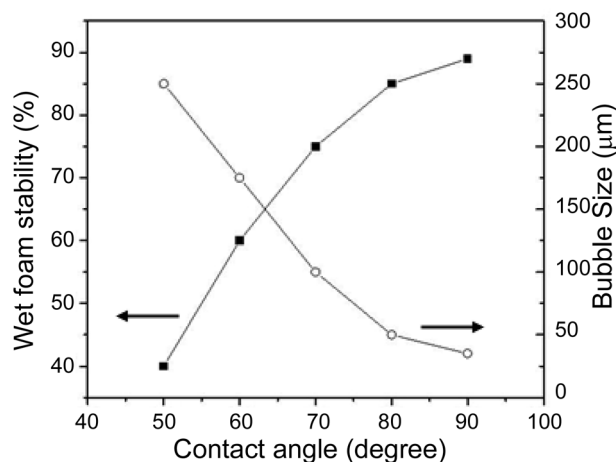


Fig. 4. Wet foam stability and bubble size with respect to suspension contact angle before foaming.

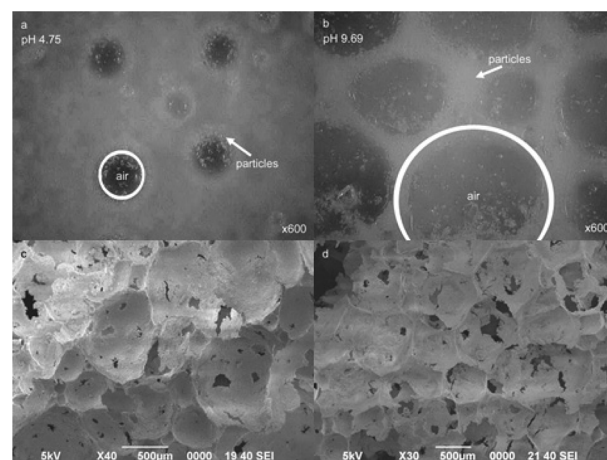


Fig. 5. Images of wet foam (a, b) viewed under optical microscope and SEM image of solid foam(c-at 0.1 M, d-at 0.01 M) after sintering at 1200°C.

respectively and (c, d) shows the pores and distribution in different amphiphile concentrations under SEM after sintering.

4. Conclusion

Concentrated colloidal alumina particles were rendered hydrophobic *in situ* by propyl gallate, facilitating the preparation of high-volume wet foams with air contents of up to 82% and bubble sizes of c.a 50~300 μm . The foams show neither bubble growth nor drainage over days. The degree of induced hydrophobicity was adjusted through varying the concentrations of the particles in the initial suspension.⁹⁾ The adsorption of these modified particles to air-water interfaces significantly reduced the surface tension of the suspension. Contact angles were sufficiently high to demonstrate that the alumina particles were made partially hydrophobic by the addition of the amphiphile. When the particles' surfaces were sufficiently hydrophobic, the suspensions foamed homogeneously throughout. The resulting highly stable wet foams could be dried in air without bubble coarsening or cracking. The porous ceramics obtained after sintering exhibited porosities of up to 80%, with either open or closed cells of c.a 30~300 μm .

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