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ScienceDirect
Journal of the European Ceramic Society 27 (2007) 879–885
www.elsevier.com/locate/jeurceramsoc

Effects of powder characteristics, solid loading and dispersant on bubble content in aqueous alumina slurries

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Available online 5 June 2006

Abstract

Bubbles occurring in ceramic slurries usually result in formation of abnormal pores in the subsequently consolidated green samples, thus deteriorating the properties of the final ceramic product. In this work, bubble content and its stability in aqueous alumina slurries were investigated with applying vacuum deairing. The experimental results show that the powder characteristics and solid loading greatly affected the bubble stability in the slurries and thus determined the bubble content. The bubble content was obviously increased with increasing solid loading, as well as using powders of high specific surface area in both as-prepared and deaired slurries. The stabilization mechanism of air bubbles in the slurries is attributable to the enhanced hindrance effect on bubble uprising caused by dense particle arrangement in slurry bulk, and the increased strength of bubble films at the slurry surface.

Keywords: Suspensions; Air bubble; Porosity; Strength; Al_2O_3

1. Introduction

Heterogeneities or defects are the main cause of deteriorated properties and low reliability in ceramic components.[1,2] During recent years, colloidal processing has attracted a growing interest due to its potential in reliably producing ceramic products through careful control of initial ceramic slurries.[1–4] For a variety of forming techniques, preparing well-dispersed slurries and retaining the homogeneity in the subsequently formed green bodies are the key issues for achieving high reliability of sintered parts with desired properties. However, air bubbles are inevitably introduced during slurry preparation at the present handling conditions. Even though a routine deairing step is commonly taken to avoid large defects caused by entrapped air bubbles, the result is not sufficiently satisfactory, since dense slurries, especially those with fine powders, are generally preferred, where bubbles are difficult to be removed completely.[5–8] There is still lack of clear understanding of bubble occurrence and bubble behaviors in ceramic slurries, though it is necessary for optimum slurry control.

Based on the above background, bubble formation in aqueous alumina slurries was studied in our recent work.[9] It was found that the bubble contents in as-prepared slurries are greatly affected by alumina particle characteristics and solid loading. Combined effect of the two factors was interpreted by introducing a new parameter, A_i, solid surface area per unit volume slurry. Bubble content increases with increasing A_i. The aim of the present work is to further study bubble stability in slurries under vacuum deairing condition concerning the effect of powder, solid loading and dispersant. Moreover, the effect of entrapped air bubbles on the green and sintered density and the final strength were also investigated with applying a novel forming method "floc casting", which is based on the temperature-induced flocculation of slurries as reported in the previous work of our laboratory.[10] This forming method has the advantages over the common gel casting by in situ flocculating the dispersed slurries without a further addition of monomer and cross-linker and offer the potential to obtain homogeneous, dense and near-net shaping samples.

2. Experimental procedure

The commercial submicron α-alumina powders AL-160SG-1 (Showa Denko Co., Japan) and AKP-20 (Sumitomo Chemistry Co., Japan) were used in this study. The mean particle sizes and the specific surface areas are given in Table 1. Various slurry formulations with varied solid loadings and dispersant concen-

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0955-2219/$ – see front matter
doi:10.1016/j.jeurceramsoc.2006.04.083

Table 1
Typical parameters of the alumina powders

Type	Mean particle size (μm)	B.E.T. specific surface area (m^2/g)
AL-160SG-1	0.45	7.0
AKP-20	0.57	4.0

trations were used for sample formation. All slurries were prepared in plastic bottles by mixing powders with ion-exchanged distilled water and a commercial dispersant D-305 (Ammonium polyacrylate, Chukyoyushi), followed by milling with alumina balls for 24 h. Bubble content were measured by sampling from the center of the bulk slurry and calculated according to the following equation:

$$C_b\,(\%) = \left(\frac{1-\rho}{\rho_0}\right) \times 100, \tag{1}$$

where C_b is the bubble volume fraction, ρ the slurry density (measured with pycnometers) and ρ_0 the theoretical slurry density without bubbles (determined by the slurry composition). All the measurements were carried out at 26–28 °C.

Slurries with different solid loadings for the two powders were used for the vacuum deairing. Herein the amounts of dispersant added for AL-160SG-1 and AKP-20 slurries were 0.5 and 0.4 wt.%, respectively. Deairing was performed by mechanically stirring 200 ml slurry in a stainless steel container under a vacuum of about 0.03 atm. The vacuum was obtained with a water flow pump, which can assure a certain water vapor pressure to minimize the surface drying of the slurry. Bubble contents of the deaired slurries were measured with varied deairing times.

The AL-160SG-1 slurries (50 vol.% solid loading and 0.5 wt.% dispersant) with different deairing times were formed into compact to examine the effect of entrapped air bubbles on density and strength of formed ceramic bodies. The slurry was firstly poured into a rectangular resin mold (50 mm × 70 mm × 30 mm), sealed, and then heated to 85 °C at 1 °C/min and kept for 1 h, by which the flocculation took place resulting in consolidation of the slurry. The sample was demolded after slowly cooled down, and followed by controlled drying. A pre-sintering at 1000 °C for 30 min was conducted to get an enough handling strength of the green sample. The final sintered sample was obtained by sintering the green sample at 1580 °C for 2 h.

Archimedes method was used for determining the bulk density of the samples. The pore structure in the green samples was examined with an immersion liquid method in the transmission mode under an optical microscope.[11] Flexural strength measurement was performed on JIS 1601 bending test machine using specimens with dimension of 3 mm × 4 mm × 35 mm cut from sintered compacts. Surface tension of the dispersant-water solution and all the slurries were measured at 25 °C using DuNouy ring method to examine the effect of alumina particles and dispersant on bubble stability on the top of the slurry. Ion-exchanged distilled water was used as a standard sample. Viscosity of the slurries was measured with a rotary viscometer (Visco-BL, Tokimec Inc., Tokyo, Japan). Ion-exchanged distilled water was used as a standard sample. Flow chart of the experimental procedure is illustrated in Fig. 1.

3. Results

Fig. 2 shows the change of bubble content in AL-160SG-1 and AKP-20 slurries with the different deairing times. An abrupt decrease of bubble content is found within 5-min deairing for both the two types of slurries, while no significant change is shown with prolonged deairing time up to 30 min. The residual bubble contents are about 0.4 vol.% for AKP-20 and 0.8 vol.% for AL-160SG-1, corresponding to about half of the values of as-prepared slurries, respectively.

Fig. 3 shows the pore structure of the green samples (AL-160SG-1) optically observed by applying an immersion liquid method. Many large pores with the sizes up to a few hundreds μm can be observed in the green body formed from the slurry without deairing (Fig. 3(a)). A relatively uniform morphology with noticeable decrease in the density and the size of pores has been found in samples with only 1-min deairing (Fig. 3(b)). A similar morphology with presence of some small pores was also observed for samples with prolonged deairing times (Fig. 3(c) and (d)). Although the observation is hardly to distinguish the difference among the deaired samples, it does confirm that deairing is very effective and efficient to diminish the defects (pores with size from tens to a few hundreds μm) in the ceramic green bodies. On the contrary, it is also indicated that the bubbles are difficult to be eliminated completely in the present vacuum deairing condition. This result is in agreement with the fact that the residual bubble content in the alumina slurries has little change with increasing time after the 1-min deairing.

Density and strength measurements reveal a great change in the properties of green and sintered bodies before and after the slurry deairing. The results are given in Fig. 4. Both the green and sintered densities were enhanced and reached a maximum after 5-min deairing of the slurries, and then negligible change was found with prolonged deairing time to 30 min (Fig. 4(a)). Correspondingly, the flexural strength of sintered samples is in good accordance with the respective density (Fig. 4(b)). The average strength firstly increased from 150 MPa (without deairing) to 360 MPa (1-min deairing), and then up to around 400 MPa for both 5- and 30-min deairing cases. These properties are closely related to the change of bubble content in slurries (Fig. 2) and pore defects in green bodies (Fig. 3). The experimental results proved that the properties of ceramic products are very sensitive to the defects caused by entrapped bubbles during slurry processing.

Fig. 5 shows the influence of solid loading on bubble contents in as-prepared and deaired slurries. The deairing time is 5 min. For both types of alumina powders, the bubble contents in the slurries increase with the increased solid loadings with and without deairing. Note that the AL-160SG-1 slurries always contain higher bubble content than the AKP-20 slurries at the same solid loading.

Fig. 6 illustrates the effect of dispersant concentration on bubble content and viscosity of the slurries. It is shown that the variation in dispersant concentration (0.4–0.7 wt.%) has negligi-

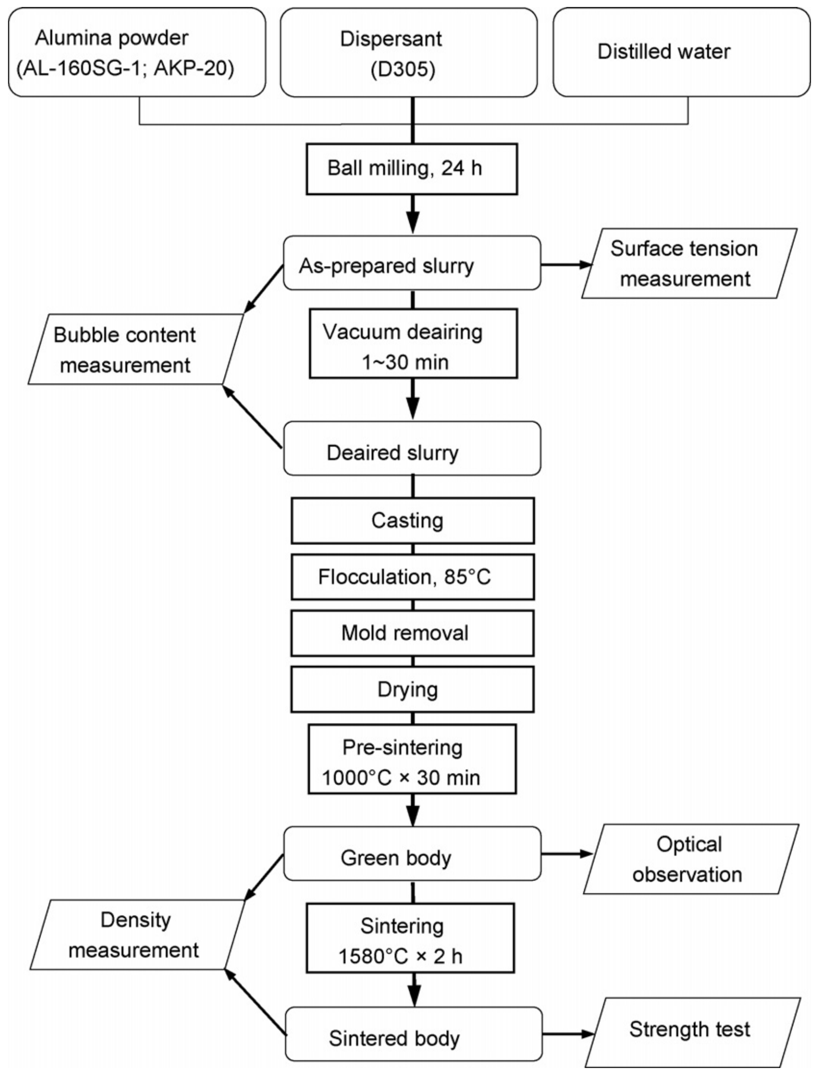

Fig. 1. Flow chart of experimental procedure.

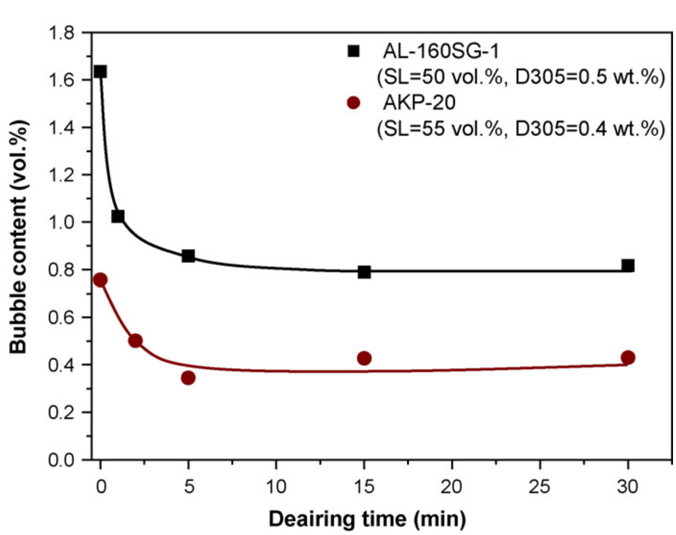

Fig. 2. Effect of deairing time on bubble content.

ble influence on the bubble content (Fig. 6(a)) as compared with that of solid loading (Fig. 5), though it may obviously affect the viscosity of the slurries (Fig. 6(b)).

Based on the results in Figs. 5 and 6, the bubble content in as-prepared and deaired slurries could be plotted as a function of A_i, as summarized in Fig. 7. The parameter $A_i(=\rho_p C_s A)$ is solid surface area per unit volume slurry (ρ_p is the density of alumina powder, C_s the solid loading, and A is the specific surface area of alumina powder).[9] It is found that bubble content increases with increasing A_i of slurries, whenever deaired or not.

The surface tensions of AL-160SG-1 and AKP-20 slurries with varied solid loadings and dispersant concentrations are shown in Figs. 8 and 9, respectively. Surface tension is a measurement of the cohesive energy present at a liquid–air interface. Here we measure the 'surface tension' of the slurry system when alumina particles are dispersed in the water-dispersant solutions. This 'surface tension' virtually represents the force required to break a film of 1 cm length, by which we could evaluate the stability of a bubble film during vacuum deairing. It indicated that

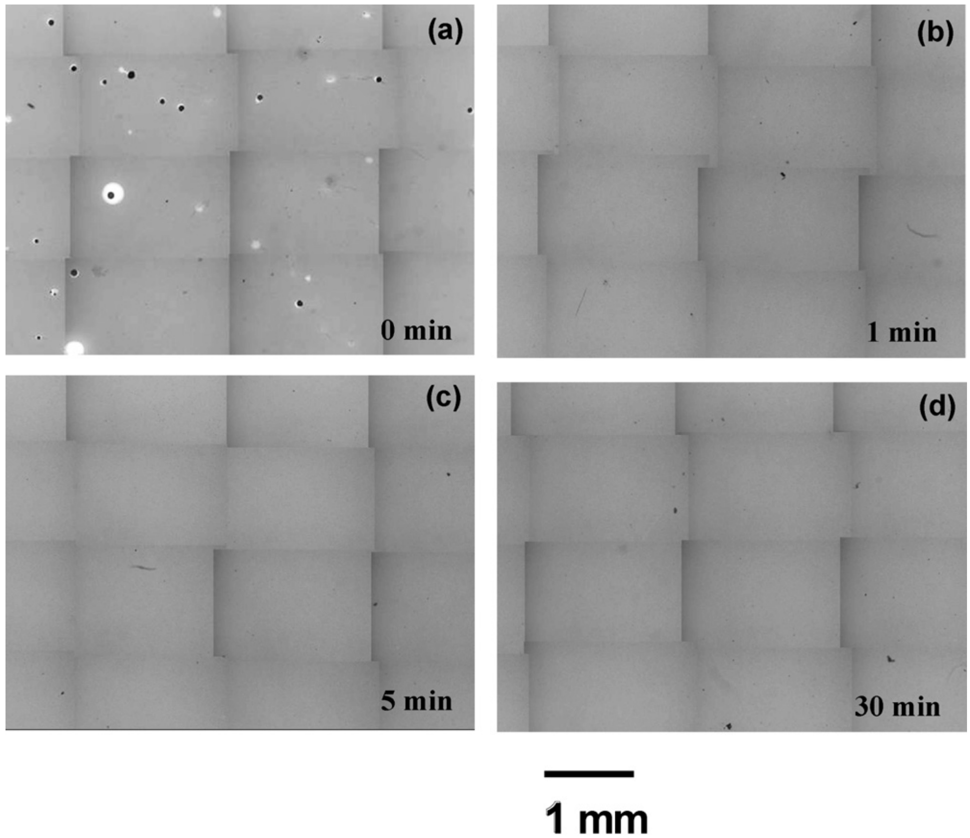

Fig. 3. Pore structure of AL-160SG-1 green samples with increasing deairing time, observed with immersion liquid method under optical microscope. The solid loading is 50 vol.%, and the dispersant concentration 0.5 wt.%.

the presence of alumina particles produces an increase in the surface tension of the water-dispersant system (Fig. 8). Similar phenomenon has been also reported recently.[12] Furthermore, surface tension increases with increasing solid loading and is higher for the AL-160SG-1 slurries as compared to the AKP-20 ones at the same solid loading. However, the variation of dispersant concentration seems to have little effect on the surface tension (Fig. 9(a)) though the dispersant D305 actually lowers the surface tension of water to some extent (Fig. 9(b)). Again, the data of surface tension of different slurries are summarized with respect to a change of A_i value of slurries as shown in Fig. 10. It is found that a higher A_i value resulted in a higher slurry surface tension.

4. Discussion

The air films existing on the powder surfaces are the main source of bubble introduction during slurry preparation and air bubbles entrapped in alumina slurries are relatively stable.[9] After slurry preparation, some big bubbles are usually observed on the top of the slurries, and their stability is dependent on the stability of bubble film. Note that the bubbles concerned in this study are far from these apparent big bubbles, but those “dispersed” small ones invisible to naked eyes since the experimental sampling was taken from the bulk of slurries. The existence of large amount of small “dispersed” bubbles is affirmed by the fact that drastic expansion of slurry was observed during vacuum deairing especially for slurries with high solid loadings. Therefore, the mechanism of bubble stabilization could be discussed from two aspects—bubble stability in the slurry bulk and at the slurry surface.

Once a bubble forms in slurry, its motion depends on the balance between the buoyant rise force and the drag force it experienced. The magnitude of buoyant rise force is proportional to the dimension of bubble. The drag force is mainly resulted from hindrance effect of alumina particles. A bubble can stay stably in the slurry only when the drag force surpasses the buoyant rise force.

As indicated from our experimental results, the bubble content largely depends on powders characteristics (particle size distribution and shape that determine the specific surface area) and their quantity (solid loading) in slurries (Figs. 5–7). That is to say, bubble stability is closely related to the A_i value that reflects the particle arrangement in slurries and is determined by the specific surface area of powder and solid loading. The higher the A_i value, the denser the particle arrangement structures in slurry, and the stronger the hindrance force of particles to bubble uprising. Therefore, slurries with higher A_i values facilitate the existence of bubbles with bigger size (with bigger buoyant rise force) or larger quantity in slurry bulk, in addition to the possibility of introducing more air films from the initial powder surfaces. This explains why AL-160SG-1 slurries contain

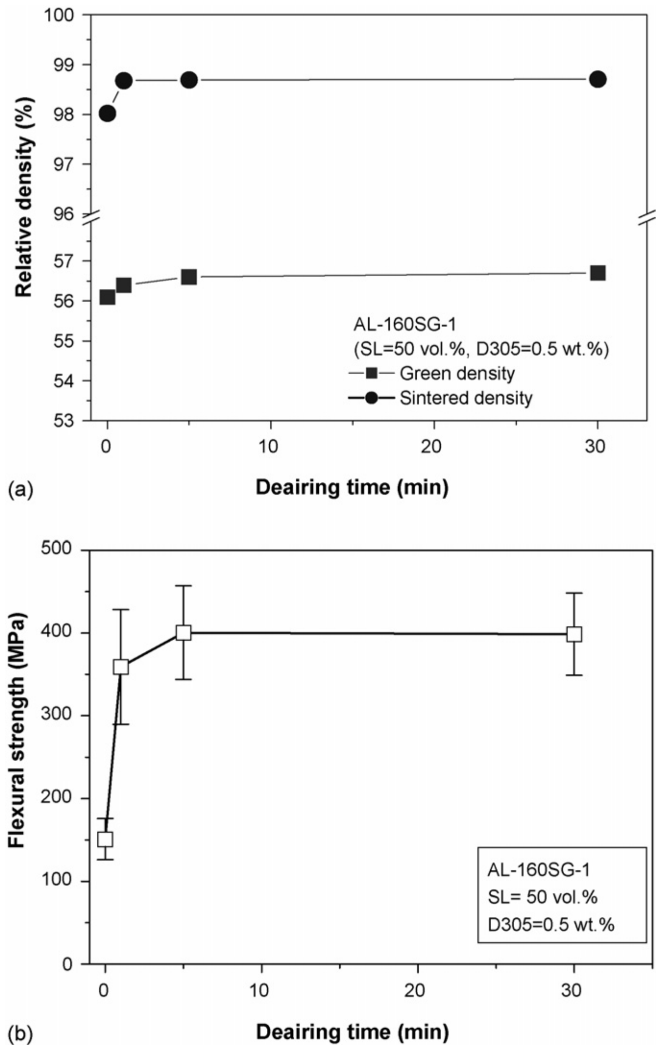

Fig. 4. Effect of deairing time on (a) green and sintered densities, and (b) flexural strength of AL-160SG-1 compacts.

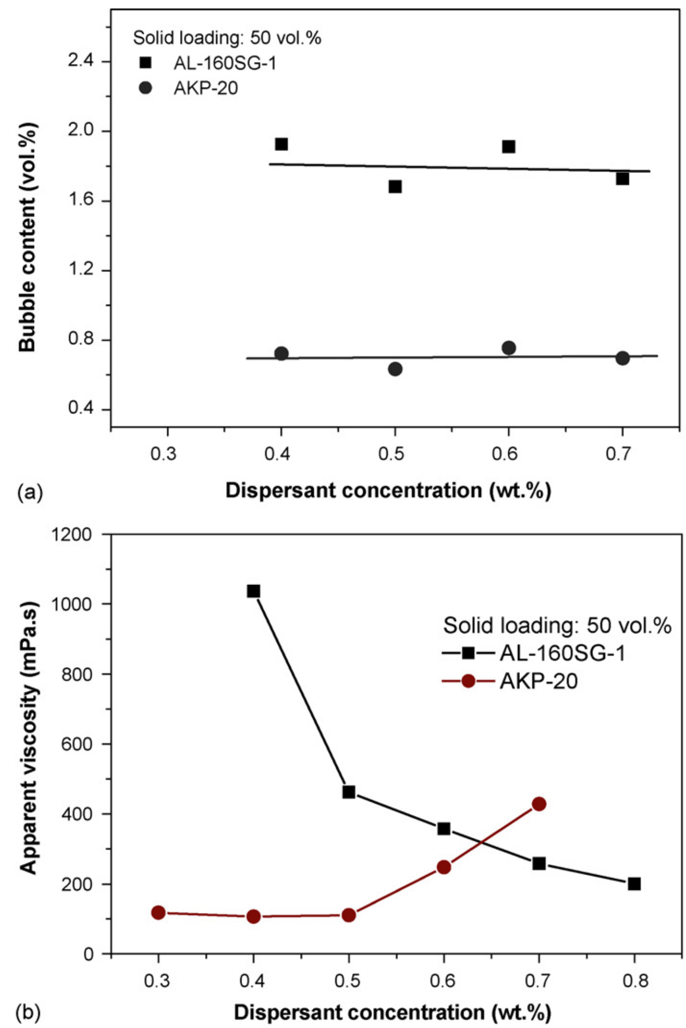

Fig. 6. Effect of dispersant concentration on (a) bubble content and (b) viscosity (at a shear rate of $10\,s^{-1}$).

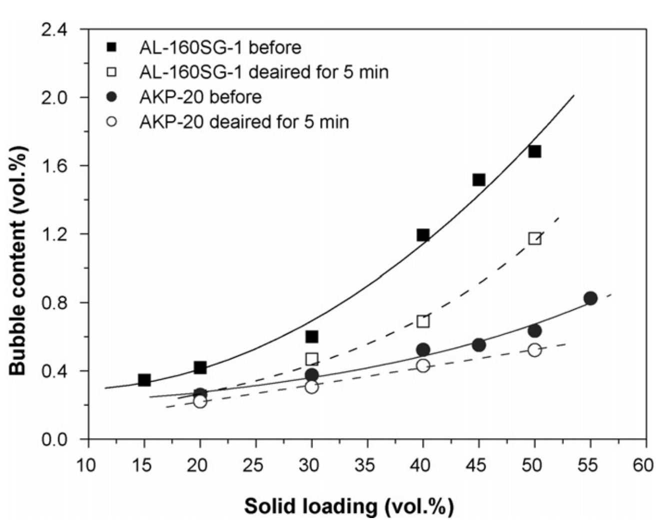

Fig. 5. Effect of solid loading on bubble content.

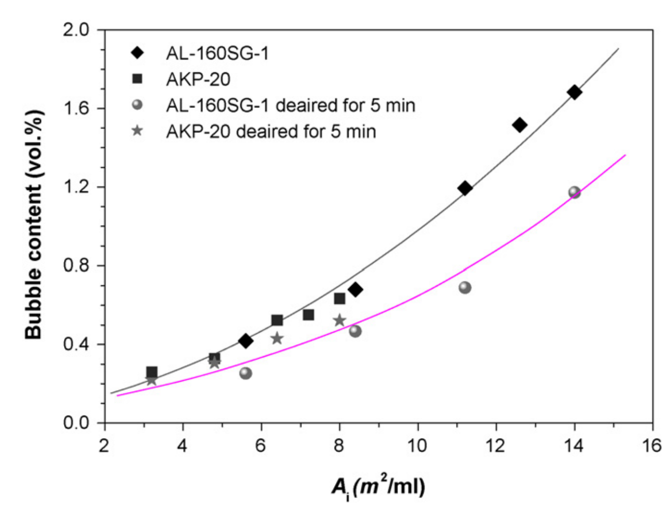

Fig. 7. Effect of solid surface area per unit volume slurry (A_i) on bubble content.

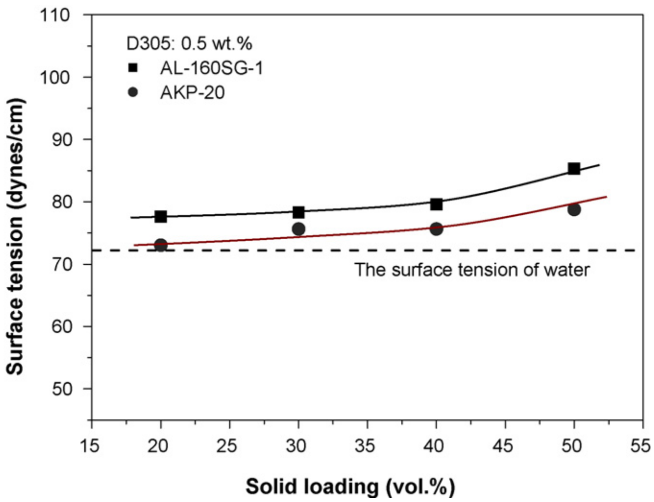

Fig. 8. Surface tension of AL-160SG-1 and AKP-20 slurries with different solid loadings.

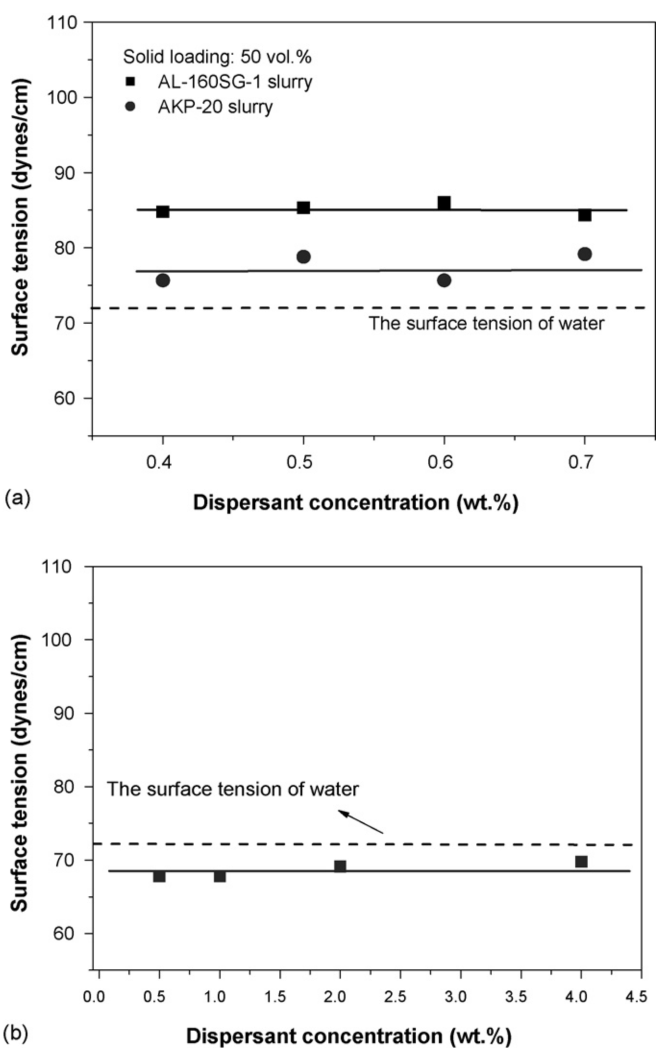

Fig. 9. Surface tension of (a) alumina slurries and (b) dispersant-water solution with varied dispersant concentrations.

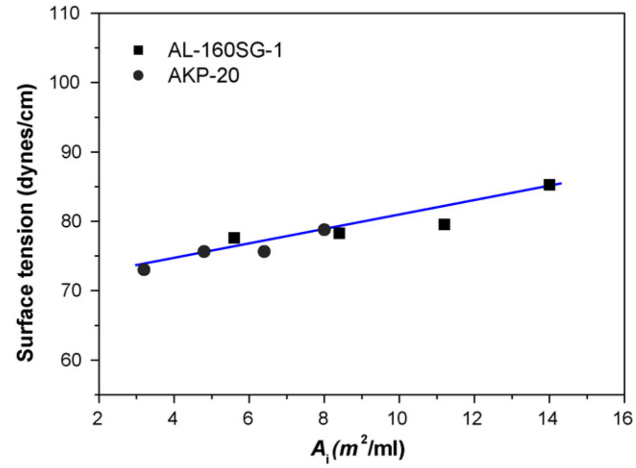

Fig. 10. Effect of solid surface area per unit volume slurry (A_i) on surface tension of slurries.

higher bubble content than AKP-20 slurries and the bubble content increases with increased solid loading in as-prepared slurries (Fig. 5).

During the vacuum deairing, the bubbles in slurry expand quickly because of the abrupt decrease in the outer pressure. The previous balance between the buoyant rise force and the hindrance force is broken so that most of the bubbles can float to the top of the slurry due to increased buoyancy after their expansion. Therefore, an abrupt decrease of bubble content was observed after a short period of deairing within 5 min. However, some originally small bubbles are still smaller than the critical size for uprising, thus lead to the residual bubble content in the slurries with prolonged deairing time. This has been proved by the fact that very small pores still remained in the green bodies after the slurry deairing up to 30 min (Fig. 3). Furthermore, higher A_i suppresses more strongly the expansion and coalescence of bubbles and thus impedes bubble uprising. Therefore, slurries of a higher A_i value, i.e. higher specific surface area of initial powder and/or higher solid loading have a higher residual bubble content after deairing.

As a bubble rises at the slurry surface, new surface is created as a result of formation of hemispherical bubble film. Bubble stability at the surface of the slurry can be evaluated by the surface tension of slurry since the surface tension indicates the energy needed to create a new surface. The experimental results confirmed an increase in surface tension of slurry with increasing A_i (Fig. 10). Thus the bubble stability at the slurry surface is also enhanced with increasing the A_i that improves strength of bubble films. The stabilization of powder on bubble films at slurry surface is favored by the increased energy barrier due to the denser particle in-layer structure of the film by higher A_i.[13,14]

As for the insignificant influence of the dispersant on bubble content, it is speculated that some competing factors were in effect. A deficit or surplus of dispersant in a slurry system could cause a certain degree of slurry flocculation, thus resulting in an increase of the viscosity. Bigger bubbles may be entrapped in the powder agglomerates (due to the flocculation); nevertheless, bubbles locating in the space between the agglomerates could uprise more easily due to the enlarged inter-agglomerate distance by the flocculation. Furthermore, the dispersant variation also has little influence on the stability of bubbles at the slurry surface, as indicated by the little change in surface tension of the slurries (Fig. 9(a)). As a result, the change of bubble content was insignificant by the variation of dispersant. Therefore, it is more feasible to use the parameter of A_i other than viscosity as a criterion for evaluating bubble stability in the slurries with relatively good dispersability. The well-dispersed slurry system is preferred in practical ceramics processing.

In summary, stability of air bubble both in the bulk and at the surface of aqueous alumina slurries is increased with higher A_i. Therefore, the influence of powder type and solid loading on bubble content should be considered in practical slurry processing in order to improve the qualities of ceramic products.

5. Conclusions

Alumina powders of high specific area and high solid loadings lead to high bubble content both in as-prepared and deaired slurries. The combined effects of these two dominant factors on stability of bubble in alumina slurries were interpreted by introducing a parameter, A_i, solid surface area in per unit volume slurry. Increase of A_i value, corresponding to increased specific surface area of initial powder and solid loading, causes denser solid particle arrangement and enhanced surface tension of slurry. Consequently, the bubble content is increased due to impeded uprising of bubble in the slurry as well as stabilized bubble films at the slurry surface. The polyelectrolyte dispersant used here has little effect on bubble content in the slurries.

Acknowledgement

This work is supported by the 21st Century COE (Center of Excellence) Program from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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