Relationship between Foam Stabilization and Physical Properties of Particles on Aluminum Foam Production*

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Experimental investigation of the foam stabilizing factors that influence aluminum foam fabrication is crucial to improve the foaming process. Solid particles contribute to an increase of the viscosity of the liquid phase and overall foam stability. Foam stability depends on the liquid type, wettability and the shape of solid particles. Even though a poor wettable particle contributes effectively to enhance liquid viscosity, the particle leads to the collapse of the foam cell due to the poor energy balance at the interface between the solid and the liquid. In our study, the effect of particles was investigated using both water solutions and aluminum melts. We show that not only the relative viscosity, but also the physical properties of solid particles need consideration during aluminum foam production. [doi:10.2320/matertrans.F-M2011817]

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1. Introduction

Closed cell aluminum foams contain significant numbers of pores. The porosity of the foams is in the range of 80–90 vol%. The foam material has numerous desirable properties, such as, light weight, high energy and good sound absorption. Thus, the materials have great potential for application in various industrial fields. Recently, increased research activity can be observed in the transportation industry applications for the purpose of weight reduction and the corresponding reduction in environmental load. However, aluminum foams have not achieved wide practical use due to the high production cost and lower strength.

It is well known that the mechanical properties of aluminum foam depend on diameter, uniformity and shape of the pores and the cell wall thickness. One can achieve higher strength if the cells are smaller and have a uniform distribution. Thus, foam architecture control (geometry and distribution) during manufacturing and alloy composition can lead to stable foams which can prevent foam collapse and coalescence, up to the end of the solidification. Stable foam requires high viscosity and low surface tension. The high viscosity contributes to slow the rate of liquid drainage caused by gravity and low surface tension acts to decrease the critical cell wall thickness when collapse occurs. However, the surface tension of an aluminum melt is around 14 times higher than that of pure water, and the addition of bismuth, as a surfactant, decreases the surface tension to the half of the original value and does not result in a stable foam. During an Alporas type foam production, a viscosity increasing process called thickening is applied, by in situ production of Ca containing oxide particles, via air injection into the melt. As the thickening proceeds, more solid particles are created in the melt making a foamy high temperature suspension. The parameters of the thickening are key elements of aluminum foam production technology.

Until now, the foamability of a suspension has been investigated using water solutions. The reports reveal experimentally, that the addition of solid particles into water solution can lead to stable foam formation. However, the influence of particle properties (like wettability) on the stabilization is still under discussion. In addition there are only a few experimental works on the stabilization of metallic melts due to the high temperature and opacity.

The aim of this work is to clarify influencing factors on both foam stabilization and thickening of suspension based foams, which contain various types of solid particles, both in water and an aluminum melt. The thickening efficiency and the stabilization of foams were evaluated using single film experiments of water solutions containing various solid particles. Aluminum foams were also produced in order to investigate the effect of the solid particles on foam stabilization and foamability.

2. Experimental Procedure

2.1 Viscosity and foam film stability of water suspensions

Al₂O₃, MgO and SiO₂ solid particles with different diameters and shapes were added into water including 0.2 mass% of sodium oleate using a magnetic stirrer. All of the water solutions were added 0.2% of sodium oleate since it was difficult to make foam films without surfactant. As shown in Fig. 1, both shapes of sphere and rough were applied in the case of Al₂O₃ and SiO₂ particles. Besides, only rough shape was used in the case of MgO particle. Table 1 indicates the physical properties of the particles. The contact angles were measured by a sessile drop technique using solid ceramic plates and two type of liquids, namely pure water and water solution including 0.2 mass% of sodium oleate.

The viscosity was measured using a tuning fork viscometer (A&D Co. Ltd., SV-10, range: 0.3–10000 mPa, accuracy: ±1%) immediately after the stirring process ended, in order to eliminate the effects of gravitational sedimentation of the
particles. The viscometer was calibrated using standard viscosity liquids before each measurement.

The collapse time of the foam film was considered as the evaluation factor for the foam stabilization of the suspension, as a function of the volume fraction and the physical properties of the solid particles. The aqueous experiments were performed under a 100% humid atmosphere using a glove box and a humidifier in order to prevent water vaporization during the experiments. A 20 mm diameter stainless wire ring was inserted into the suspension and then pulled up. After this, the collapse time (lifetime) was measured while the ring was held in a horizontal or vertical position normal to gravity. The average value was calculated from five trials.

### 2.2 Production of aluminum foams

The Alporas process has three steps. During the first step, an aluminum melt is thickened by in-situ dispersion of solid particles. As a next step, a foaming agent that decomposes the gas at high temperature, is added into the melt and then mixed. In the last step, the melt is held at high temperature to induce the foaming by the released gas from the foaming agent.1,2,8)

In the case of the aluminum melt, the evaporation of the melt is low, due to a low vapor pressure. Thus, the environment does not affect the results.

We investigated various pretreated matrix materials. Metal matrix composite including 20 vol% of SiC particles (Duralcan, F3S20S, particle diameter: 12 μm) and both thickened samples of pure aluminum and Al-1.5 mass% Ca alloy were used. During the thickening treatment, the melt was stirred for 20 min at 700°C under an ambient atmosphere for the in-situ formation of oxide particles within the melt.13) Figure 2 shows the cross sections of the matrix materials. SiC particles in the composite material, oxide particles in both pure aluminum and Al-1.5 mass% Ca alloy are confirmed in the matrix. These particles remained intact and stable within the melt, at 700°C and without any significant reaction within the melt and they contribute to a viscosity increase.10,13)

Stirring torque of the melt suspension was measured as the viscosity parameter, since there is a correlation between them.14) The measured values were 0.18 Nm of the thickened pure aluminum, 0.40 Nm of the thickened Al-1.5 mass% Ca Alloy and 0.48 Nm of the composite respectively.

TiH₂ powder (Toho Titanium Co. Ltd., 99.7%, nominally < 45 μm) was applied as a blowing agent and pretreated by

| Table 1 Physical properties of added particles into water based liquid foam films. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
| Density g/cm³ | Diameter μm | Shape | Contact angle |
|                  |                  |   | water | SLS add |
| SiO₂             |                  |   |   |   |
| 2.20            | 0.9             | sphere | 15° | 4° |
| 2.32            | 1.8             | rough |   |   |
| MgO             |                  |   |   |   |
| 3.65            | 0.7             | rough | 58° | 31° |
| Al₂O₃            |                  |   |   |   |
| 3.99            | 0.3             |   |   |   |
| 3.30            | 1.1             | sphere | 45° | 30° |
| 3.99            | 3.0             | rough |   |   |

Fig. 1 SEM images of the added particles into water based liquid foam films. (a) 0.9SiO₂ (sphere), (b) 1.8SiO₂ (rough), (c) 1.1Al₂O₃ (sphere), (d) 1.0Al₂O₃ (rough).
heating to 150°C and held for more than 24 h to avoid moisture absorption.15) The 1.5 mass% of TiH₂ powder, wrapped in an aluminum foil for a good yield and mixed with 50 g of the matrix materials, melted at 700°C and stirred for 100 s. After this, the foaming of the melt was induced by holding in a furnace for 100–500 s and then the melt was quenched into water to freeze the foam architecture.

The metal foam samples were cut along the foaming direction (the opposite direction of gravity) and polished using up to 0.04 μm colloidal silica. Macro and microstructure analysis were carried out using optical microscopy and scanning electron microscopy set up with electron dispersive X-ray spectrometer. To determine a foamability parameter, quantitatively, both cell wall thickness and pore size distribution were measured. The thinnest cell walls were measured and averaged along horizontal lines in the function of the height at each centimeters (Fig. 12) from the sample bottom.

3. Result and Discussion

3.1 Viscosity and foam film stabilization of water based suspensions

3.1.1 Influence of solid particles on the viscosity of suspensions

Figure 3 shows the relationship between the addition of solid particles and the measured viscosity of suspensions. “S-” and “R-” indicate sphere and rough shapes of particle, respectively. Regardless of the type and geometry, the viscosity value increased with an increased amount of particles. This tendency can be confirmed in the case of rough MgO particles, a smaller diameter particle leads to sufficient viscosity using a lesser amount of material. This tendency can be confirmed in the case of rough Al₂O₃ (0.3, 1.0 and 3.0 μm) and sphere SiO₂ (0.9 and 8.0 μm). Therefore, smaller particles have the advantage of increasing the viscosity of the suspension under identical particle geometry and type. However, to obtain similar viscosity values, more additive is required, if the geometry different but the particles are the same, compare Al₂O₃ (R-1.0 μm vs S-1.1 μm) and SiO₂ (R-1.8 μm vs S-0.9 μm) in Fig. 3.

The relative viscosity of the suspensions can be described using the formula (1) proposed by Zettlemoyer et al.16) This formula was improved by Einstein’s viscosity formula, taking into account the volume fraction $V_C$ and surface area $A$.

$$\eta_c = \eta_0[1 + K_1(1 + K_2 A)V_C]$$

where, $\eta_c$ is the relative viscosity value, $\eta_0$ is an initial viscosity value of the liquid and both $K_1$ and $K_2$ are constants. This formula reveals that large surface areas and high volume fractions of solid particles contribute to a higher viscosity in suspensions. Thus, it can be assumed that suspensions which include spherical or large particles indicate a low viscosity since the surface areas of those particles tend to be smaller as shown in Fig. 3. The influence of particle geometry on viscosity is significant and has to be considered.

If we compare suspensions that contain similar geometries and diameters of the particles (S-1.1 μm Al₂O₃ with S-0.9 μm SiO₂), the addition of the Al₂O₃ leads to a more viscous suspension, compared to SiO₂. The physical difference between these particles is the density and the contact angle. The contact angle of SiO₂ with a water solution is smaller.

![Fig. 2 Microstructures of matrix materials of aluminum foams.](image1)

![Fig. 3 Influence of particle addition on viscosity of water based surfactant containing liquids. “S-” and “R-” indicate sphere and rough shapes of particle, respectively.](image2)
than that of Al$_2$O$_3$ as it is indicated in Table 1. However, the particles never settled to the bottom of the mixer and the particle dispersion was kept uniform during the viscosity measurement. Thus, the influence of particle density is not significant. The difference in viscosity increase tendency can be caused by the adhesiveness between the phases of solid and liquid due to the difference in contact angle (wettability).

### 3.1.2 Influence of holding direction on the stabilization of liquid foam films

Figure 4 shows the lifetime of liquid films in each orientation. S-0.9 μm SiO$_2$ particle was used for these measurements. Horizontal position indicates a longer lifetime than the vertical and the difference become larger with increasing viscosity. The cell wall often acts as a draining path within the foam, and the liquid phase easily settles due to gravitational force. This drainage induces the thinning and the collapse of cell walls over time. In the case of a few hundred nanometer thick cell walls, the drainage is also accelerated by a suction pressure caused by the curved cell wall.\(^5\)

The foam film with curved surface has a pressure difference $\Delta P$ for the vapor and the liquid phases at the interface. This pressure depends on the surface tension and the curvature and can be described by the following formula (Young-Laplace formula)\(^5\)

$$\Delta P = \frac{2\gamma}{R}$$

(2)

where $\gamma$ indicates surface tension, $R$ is the curvature radius in meters and $\Delta P$ is called capillarity pressure or Laplace pressure in Pascals. This formula shows that at large curvature liquid tends to move toward the small curvature to decrease the pressure, if one cell wall is composed of various curvatures. The suspension viscosity have only a slight influence on the cell lifetime.

In case of the horizontal orientation, as indicated in Fig. 5, liquid within the foam film flows to the center and the film became concave. Conversely, vertical positions cause the film to drain at the bottom since the draining path and gravity are parallel. In addition, the curvature difference of the surface of the film held vertically became larger, thus, the draining rate can be accelerated by suction pressure of a neighboring film as represented in formula (2).

Form these results, it can be assumed that gravity forces parallel to cell walls collapse more easily within the foam, since the lifetime of the foam film held vertically is significantly shorter. Therefore, we concentrated our research to vertical measurements.

### 3.1.3 Influence of solid particles on foam film stabilization of water solutions

The lifetimes of various particles containing suspension foam films are shown in Fig. 3. The film containing smaller particle has a longer lifetime using similar geometry and type of particles. The shape of the particles also has an influence on the foam film stability. Comparing the measurement data of the R-1.8 μm and S-8.0 μm SiO$_2$ particles and the R-0.3 μm and S-1.1 μm Al$_2$O$_3$ particles we found an increase in film lifetime if the particles were spherical. In addition, 0.9 μm SiO$_2$ particle loaded film is more stable than that of 1.1 μm of Al$_2$O$_3$.

In Fig. 6 the measured viscosity and lifetime values are compared. As we can see, the viscosity does not influence significantly, the film stability, except in case of the spherical SiO$_2$. Figure 7 shows both changes of viscosity and lifetime in the function of the particle concentration. In order to evaluate the effect of the type and the shape of the particle, S-0.9 μm SiO$_2$, S-8.0 μm SiO$_2$, S-1.1 μm Al$_2$O$_3$ and R-1.0 μm Al$_2$O$_3$ were compared.

In case of the spherical particles, both viscosity and lifetime increased with increased particle concentration for all sizes and types particles. High viscosity value and long lifetimes can be obtained by smaller additions amount of 0.9 μm SiO$_2$ rather than 8.0 μm SiO$_2$. If we compare 0.9 μm
SiO$_2$ versus 1.1 μm Al$_2$O$_3$. SiO$_2$ is more effective to prolong lifetime but Al$_2$O$_3$ is more effective to increase viscosity (shape and size of the particles are similar). It can be deduced from this observation that the pertinent factors are different if we consider suspension thickening or foam stabilization. Table 1 reveals that a significant difference of the physical properties between S-0.9 μm SiO$_2$ and S-1.1 μm Al$_2$O$_3$ is the density and the contact angle, the values for SiO$_2$ is smaller than those for Al$_2$O$_3$. Large density accelerates the draining rate in the foam films and the high contact angle impairs cohesion forces between particle and water solution. Thus, more stable foam films can be made from suspensions containing SiO$_2$.

Comparing the influence of the shape of Al$_2$O particles between R-1.0 μm and S-1.1 μm, the suspension containing 11 vol% of rough particles indicate 58.7 mPa·s (viscosity) and 78 s (lifetime), and those containing 13 vol% sphere particles shows 3.44 mPa·s and 249 s. This indicates that sphere particles prolong lifetimes significantly, despite low viscosity, therefore sphere particle has an advantage for the stable foam film formation compared to rough particles.

Suspension viscosity was considered to be the main contributing factor in foam stability until now. However, stable foam films can be made by the addition of particles which have good wettability and/or small surface areas, even though these particles are not effective as thickening agents for suspensions.

3.2 Foam stabilization of the aluminum melt suspensions

3.2.1 Macrostructure of the aluminum foams

Figure 8 shows the cross sections of aluminum foam samples. It is confirmed that pore size grows with holding time for all samples. Both the Al-1.5 mass%Ca and the composite samples have uniform pore distribution. The pure Al sample held for more than 300 s is composed of laminated layers at the top, large pores at the middle and a denser section at the bottom. The thickness of the dense layer increases with holding times. This should mean that the pores are easily collapsed by the fast drainage due to the low viscosity liquid.

Comparatively, both foams fabricated from the Al-1.5 mass%Ca alloy and the composite materials have a uniform distribution of pores. The average diameter of the pores increase with holding time and this increase is significantly more for the Al-1.5 mass%Ca than in the composite samples. In addition, the foam evolution for the samples made from the composite materials is the slowest since 100 s of holding did not induce foaming, only pore formation was started.

In order to investigate the architectural foam sequence within the samples of the Al-1.5 mass%Ca and the composite material, magnified cross sections were observed as shown in Fig. 9 and 10 respectively. In the case of the Al-1.5 mass%Ca 100 s held sample, the pore diameters and the cell wall thickness are similar within the sample and the pores are spherical (Fig. 9). The pores grow with time. Also, the pores at the top transform into polygons and those at the bottom remain spherical, which illustrates clear evidence of the existence of liquid drainage during foam evolution. This phenomenon is confirmed in the samples using composite materials as shown in Fig. 10. However, the variation in the Al-15 mass%Ca sample during the foam evolution is more significant than that in the composite sample. The value of the stirring torque are 0.40 Nm of the Al-1.5 mass%Ca and 0.48 Nm of the composite respectively. Thus, this causes the variation of difference during the evolution.

3.2.2 Pore size distribution and cell wall thickness

Foam stabilization was evaluated in chapter 3.1 as the collapse time of water suspension foam films. Due to the high temperatures and opacity, *in-situ* observation of foam evolution of aluminum melts is very complicated. In this study we carried out an *ex-situ* quantitative evaluation of the foam evolution. The cell wall thickness and the pore number per unit area were measured as a function of holding time; there are correlations between the above values and foam stability.
Figure 11 shows the cell number density. The numbers decrease with increasing holding times due to cell growth and rupture, regardless of the matrix materials. Although the cell growth of the composite foam somewhat retarded the final cell number density is similar at a 500 s holding time.

The relationship between cell wall thickness and holding time is indicated in Fig. 12. Thinner walls are distributed at the top of all samples. As the holding time elapsed, the cell wall thickness towards the bottom significantly increased and the latter value of the Al-1.5 mass%Ca sample is 12.5 μm and that of the composite sample is 34.0 μm.

The observed cell wall thickness redistribution is influenced by the drainage which contributes to the foam stability. We have found that the composite foam has higher foam stability as compared to the Al-1.5 mass%Ca sample and the foam decay of the Al-1.5 mass%Ca sample is more significant than that of the composite sample.

3.2.3 Microstructure of the cell wall

Figure 13 shows SEM images of the cross sections of the thinnest cell walls of the samples held for 300 s (Fig. 8). The pure aluminum cell wall image was not magnified since the thickness was already large. Primary α-Al phase, oxides and white precipitates are observed in the pure aluminum sample. TiH₂ powder as a foaming agent attributed to form precipitates and this justifies by the large titanium peak of the precipitates using EDS analysis (Energy dispersive X-ray analysis). In case of
the Al-1.5 mass%Ca sample, the microstructure is composed of primarily \( \alpha \)-Al phase, oxides and many intermetallics (white portion) in which aluminum, calcium and titanium were detected by EDS analysis. The melt of the Al-1.5 mass%Ca sample includes unreacted calcium remaining from the thickening step\(^{13}\) and Ti which decomposed from TiH\(_2\).\(^{15}\) The composite sample contains SiC particles (dark portion) and intermetallics (bright portion) within a primary \( \alpha \)-Al phase.

In addition, the cell walls in the pure Al and the Al-1.5 mass%Ca samples include folded oxide particles. In contrast, the cell wall of the composite sample is two or more SiC particle sizes thick.

For the detailed observation of solid particles existences (oxide, SiC) on the cell face, SEM (Scanning Electron Microscope) images of the cell wall surface are shown in Fig. 14. Both samples were prepared from the samples held for 300 s (Fig. 8). A smooth surface is confirmed for the Al-1.5 mass%Ca sample. In comparison, the surface of the composite sample indicates a rough surface geometry due to the salient SiC particles.

### 3.3 Foam stabilizing by solid particles in aluminum melt

Previous literature data reveals that stable foam films require high viscosity suspensions. Higher viscosity value can be obtained if the particle diameter is small, the contact angle is large and the surface area is large. Alternatively, our investigation indicates the particle conditions to form stable foam films are: small particle diameter, low contact angle and low surface area (spherical shape). The particle diameter effects on both the viscosity and the foam film stability but an opposite effect exists for the suspension thickening and the foam stabilization if we look at the effect of the contact angle and the particle geometry.

The composite melt foam can be considered more stable than that of the Al-1.5 mass%Ca since the former has less drainage (Fig. 12). This advantage can be originally, as a higher melt viscosity effect. However, the minimum cell wall thickness of the composite sample is larger than that of the Al-1.5 mass%Ca sample.

The oxide is located within the cell wall of the Al-1.5 mass%Ca and the pure Al samples and surrounded by the aluminum phase as shown in Fig. 13. Conversely, SiC particle are protruding from the cell wall. The oxide within the Al-1.5 mass%Ca sample, which formed with air mixing during the thickening treatment, has a folded, film geometry.\(^{14}\) The base material of the composite sample contains SiC particles.\(^{17}\) The literature states that the wettability between aluminum melts and solid ceramics is poor, namely at more than a 90° contact angle.\(^{18}\) Thus, the SiC particles of the composite material should act as poor wettable particles at high temperature. In contrast, the folded oxide films within the Al-1.5 mass%Ca sample behave as good wettable solids since they remained in the inner portion of the cell walls after the *in-situ* production and foaming.

Figure 15 indicates optical microscopic images of the thin cell wall and schematic illustrations of the cell wall morphology model. The images of the Al-1.5 mass%Ca
sample reveal that the oxides are coupled together with the matrix in the middle of the cell wall. SiC particles are distributed in the cell wall and a slight segregation towards the cell wall surfaces is also observable.

The energy balances of the solid/liquid interfaces can be described with the following formulas,

\[ \sigma_{\text{oxide/V}} > \sigma_{L/\text{oxide}} + \sigma_{L/V} \]  \hspace{1cm} (3)
\[ \sigma_{\text{SiC/V}} < \sigma_{L/\text{SiC}} + \sigma_{L/V} \]  \hspace{1cm} (4)

where the interfacial energies between solid, liquid and vapor are \( \sigma_{\text{oxide/V}} \), \( \sigma_{L/\text{oxide}} \), \( \sigma_{L/V} \), \( \sigma_{\text{SiC/V}} \), \( \sigma_{L/\text{SiC}} \), \( \sigma_{L/V} \). These formulas and the model in Fig. 15 demonstrate the assumption that the oxide contributes to the foam stabilization due to the high continuity between the liquid and the solid and the SiC particles act as the notch of the foam collapse.

Gergely et al. have investigated the foamability as a function of particle diameter and volume fraction using identical materials as we did.10,19–21 The reports indicate that the minimum value of the cell wall thickness is two to three times as large as the diameter of SiC particles in all conditions of the volume fractions and diameters which are in good agreement with our findings. They also stated that for stable foam a certain volume of SiC particles is required but they only considered the importance of the effect of the particles on the viscosity of the melt.

From these results we can derive that the distribution and the location of the particles depend on the energy balance at the solid/liquid interface. As it was shown, the solid particles which are produced by thickening, decrease the minimum value of the cell wall thickness and lead to a less stable foam. Regarding the current literature, foam stabilization has been discussed as being more dependent from the effect of the liquids viscosity. The results of our work show that a more viscous melt yields higher foam stability, but the efficiency of the foam stabilization also depends on the size, geometry and wettability of the particles.

4. Conclusions

The influence of the particle properties on suspension thickening and foam stabilizing were studied using both suspensions of water solutions and aluminum melts.

1) We observed the effects responsible for suspension thickening and the foam stabilization as the function of contact angle and the particle geometry. Thus, we suggest that it is necessary to take into account not only the suspension viscosity, but also, the shape and physical properties of particles.

2) Thinner foam films can be formed from the Al-1.5 mass%Ca samples than that from the SiC particle loaded composite samples. In the case of poor wettable particles, highly effective solid-particle thickening often contributes to form unstable foams since the interfacial phenomenon of particles depends on the interfacial energy balance between the particles and the solvent.

3) The viscosity of a suspension increases with a decreasing volume fraction and diameter of solid particles. Moreover, the viscosity, the wettability and shape (surface area) are determinant.

4) To form stable particle stabilized foams, the particles should have small diameters, good wettability and a low density.

5) To develop reliable aluminum foam production methods, an appropriate selection of the stabilizing particles and knowledge of the foam stabilization mechanism required.

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