Effect of CaCO₃ Foaming Agent at Formation and Stabilization of Al-Based Foams Fabricated by Powder Compact Technique

Aleksandra V. Byakova¹, Svyatoslav V. Gnyloskurenko²,* and Takashi Nakamura³

¹Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, 3 Krzyzhanovsky St., 03142 Kiev, Ukraine
²Physical-Technological Institute of Metals and Alloys, National Academy of Sciences of Ukraine, 34/1 Vernadsky Ave., 03142, Kiev, Ukraine
³Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980–8577, Japan

The paper presents the results obtained by in situ observation of Al-based foams formation at heating of powder compacts with calcium carbonate (CaCO₃) by comparing with those prepared with conventional titanium hydride (TiH₂). Foamable precursors comprising powder of either pure aluminium or AlZnMg-alloy were used for detailed investigation of foam evolution and stability. High temperature X-ray furnace was applied for in situ visualization of foam formation. It was identified that expansion and stability of foams with CaCO₃ are much superior to those with TiH₂. Distribution and size of solid inclusions (network of oxide remnants, particles of foaming agent, secondary reaction products, and solid oxide skin) in the cell wall materials of studied foams as well as relevant wetting data were determined to clarify the difference in foams stability. Improved stability of foams with CaCO₃ is explained on the base of stabilizing models developed by Kaptay by assuming an interfacial force, the disjoining pressure, which efficiency is variable and dependent on the distribution and wetting behaviour of the clustered oxide network/solid particles in foamy melt.

(Received September 6, 2016; Accepted November 28, 2016; Published January 25, 2017)

Keywords: aluminium foam, stability, X-ray observation, particle size, particle distribution, wettability

1. Introduction

Closed cell aluminium foam is a multifunctional lightweight composite material, which is currently of growing interest for design purposes in different engineering applications. However, despite a number of manufacturing processes developed for production of Al-foams the last ones contain economical and technical limitations. As applied to the frequent use methods employed for production of machinable Al-foams, which are based on handling of a melt and powder compact technique,¹⁻³ economic limitation arises due to the employment of a rather expensive titanium hydride (TiH₂) as foaming agent. Moreover, aluminium foams still suffer from non-uniformities and other structural deficiencies.

Stabilization of liquid foam, i.e. avoidance of drainage, rupture of liquid films, cell coarsening and coalescence, is believed to be an efficient way to improve cellular structure of foams and also to make process control easier and more reliable. In view of this, the application of calcium carbonate (CaCO₃) as costly effective gas-generating agent shows a lot of advantages in performance of Al-foams. Coated calcium carbonate (CaCO₃/Al₂O₃) as alternative foaming agent has been originally proposed in the development of the Alporas route⁴⁻⁵ and later applicability of CaCO₃ has been extended for Formgrip process using a precursor of Duralcan metal matrix composite (MMCs)⁶⁻⁸ and, then, for powder compact technique.²⁻⁹ The important point is that CaCO₃ as an alternative foaming agent offers a significant performance gains in view of much finer and uniform cells occurred due to the improved foam stability.⁹ Former phenomenon is currently associated with an additional stabilisation effect of oxide skin formed on surface of cell faces via the reaction of liquid Al with oxidizing CO₂ gas.⁵⁻⁶,⁸⁻¹³ Although the results related to in situ monitoring of foam formation from powder compacts being produced with TiH₂ foaming agent have been published,¹⁴⁻²¹ formation of foams created from powder compacts with CaCO₃ as gas source has not yet been systematically assessed by in situ experiments.²²

The present paper is aimed at in situ analysis of foam formation and stability at heating Al-based powder compacts with CaCO₃ by comparison with those prepared with TiH₂. Combining the in situ results with ex situ analysis of foams microstructure and also with wetting data of solid inclusions recognized in foam structure, the effort is also to clarify the effect of oxide skin at cell face and other structural parameters of foams with CaCO₃ (assigned as carbonate kind of foam) on stability of foamy melt in comparison with that indicative for foams with TiH₂ (assigned as hydride kind of foam).

2. Materials and Methods

Foamable precursors were fabricated by powder compact technique. In this process, both conventional air-atomized powder of pure Al and water-atomized powder²³ of wrought Al-Zn-Mg alloy assigned here as ZAM alloy (similar to alloy 7075) with elementary composition such as Al-5.5Zn-3Mg-0.6Cu-0.5Mn were employed in the experiments. Specification of the initial Al/Al-alloy matrix metal and powders obtained after metal atomisation with subsequent increase in oxygen content is listed in Table 1.

Powder of TiH₂ with particle size ranged from 25 to 40 μm and powder of CaCO₃ with particle size ranged from 3 to 8 μm were employed as foaming agents. Metal powder was mixed with foaming agent of 2 mass%, pre-compacted and heated to 400°C with followed extrusion in rectangular bars. A number of samples were directly machined from each kind of as-received precursors to use them for foaming experiments. Sample dimensions were about 15 × 30 mm² in square and roughly about 5 mm in height.
High temperature X-ray furnace containing vertical Al₂O₃ tube described in details previously was applied for in situ visualization of foam formation. Solid precursor with inserted thermocouple was placed on the steel supporter and introduced inside the furnace kept at 700°C under inert (argon) atmosphere. Then continuous x-ray observation was started for about 700 s, transmitted via an intensifier to CCD camera (XTV-S-420, Hitachi Medical Corporation) and recorded onto videotape. Movie was processed by PC and mean value of height of every 2 sec. images were measured showing expansion kinetics when plotted.

Wetting contact angles (θ₀) for foaming agents in contact with liquid Al were measured by immersion of solid plate made of agent material. The latter was immersed into a liquid metal disposed in mould, which was placed in furnace kept under argon atmosphere and temperature about 690°C. X-ray system with the above said furnace was used to visualize immersion contact angle (θ₀) which, then, was measured from the image of Al meniscus at solid plate when it became stable.

Calcium carbonate in a form of polished marble plate and tablet of compacted powder with mean particle size of 3 μm and titanium hydride performed by tablet of compacted powder with mean particle size about 10 μm were employed for wetting experiments.

The immersion method is effective for comparative study of wetting the foaming agents but it cannot guarantee a precise measurement of wetting contact angles of solid with liquid Al. It is known that thin Al₂O₃-oxide layer presented on Al melt surface even in inert atmosphere can interfere with direct contact of Al-melt with solid. Therefore, the improved sessile drop method was employed for precise measurements for wetting behaviour of solids in contact with liquid Al. In this method, oxide layer is mechanically stripped off the melt using a drop injection mechanism. Moreover, this technique allows clearing the solid substrate from moisture or other contaminations absorbed by its surface. Sessile drop experiments were performed in a furnace under vacuum about 2 × 10⁻³ Pa and given temperature being achieved by heating the system including solid substrate and Al melt, which is placed inside the graphite syringe with the orifice roughly about 1 × 10⁻³ m.

Structural characterization of solid precursors and foams was performed by ex situ analysis using scanning (SEM) and transmitting (TEM) electron microscopy Jeol Superprobe-733 (JEOL, Japan) and JEM 2100 F (JEOL, Japan), both equipped with X-ray detectors (EDX and EPMA).

### Table 1 Specification of matrix alloy and powders.

<table>
<thead>
<tr>
<th>Matrix alloy</th>
<th>Purity, %</th>
<th>Solidus temperature, °C</th>
<th>Melting point/liquidus temperature, °C</th>
<th>Specification of powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al 99.95</td>
<td>---</td>
<td>660</td>
<td>air &lt; 160</td>
<td>0.7</td>
</tr>
<tr>
<td>Al-Zn-Mg</td>
<td>---</td>
<td>570</td>
<td>638 water 60–100 0.6</td>
<td></td>
</tr>
</tbody>
</table>

3. Results

3.1 Foam formation and stability

Figure 1 shows the expansion kinetics for different precursors at heating. As it can be seen, three meaningful periods, i.e. solid, semisolid, and liquid state of precursor and, though, its corresponding behaviour, can be distinguished in expansion curves.

No expansion is observed below either melting point of Al precursors or solidus temperature of ZAM alloy precursors. In the semisolid state, Al samples (1,2) expand gradually while melting at constant temperature (Fig. 1(a)). Semisolid ZAM alloy precursors (3,4) demonstrate a negligible expansion at heating (Fig. 1(b)). Expansion rate for all precursors increases steeply when semisolid material is completely transformed into foamy melt at the temperature slightly above either Al melting point or ZAM alloy liquidus.

However, there are pronounced differences in evolution and stability of foamy melt created by H₂ gas released from titanium hydride and those ensured by CO₂ gas evolved from calcium carbonate. In particular, hydride kind of foam continue with expansion as temperature gradually increases above either Al melting point or ZAM alloy liquidus. On the onset of the increased temperature, hydride kind of foams (1,3) expand up to maximum values during 7 min after beginning of heating. After this the above foams runs out the expansion
and, then, decay gradually with increasing the temperature up to 700°C although release of hydrogen from TiH₂ was still in progress.⁶,⁸)

Unlike the above both carbonate kind of foam of ZAM alloy (4) and that of Al added with complex foaming agent (2) continue to expand up to the maximum values as the temperature increases up to 700°C. Finally, maximum expansion of the foams created by CaCO₃ foaming agent (2,4) is rather high in comparison with those indicative of hydride kind of foams (1,3). Moreover, the foams (2,4) keep maximum expansion for about 200 s and longer whereas hydride kind of foams (1,3) keep maximum height less than for 50 s.

X-ray images obtained in-situ at foaming ZAM precursors with different foaming agents are shown in Fig. 2 with indication of current heating time and precursor temperature.

By visual observation of these images it is also apparent that the carbonate kind of foam expands much gradually and continuously then that of titanium hydride.

Thus, the results of in situ observation indicate that CaCO₃-bearing foaming agents provide the essentially improved expansion and stability of foams compared to TiH₂. Actually, the addition of only small amount of CaCO₃ to TiH₂ provokes higher expansion of Al-based foam, as can be seen in Fig. 1 (a). This is in good agreement with the fact that foam expansion becomes higher when mixture of CaCO₃ + TiH₂ (mass ratio 1.0:0.5) was used.²⁵)

Generally, foam stability is commonly ascribed to the presence of solid inclusions, their size and fraction volume, and also wetting behaviour.¹⁶,²⁶) Therefore, ex situ observation of cell wall microstructure and cell face composition as well as corresponding wetting experiments are usually required for understanding the differences in stabilisation of two kinds of foams.

3.2 Structural characterisation of powder precursors and solid foams

The distinctive feature of powder precursors is fine oxide particles, which enter into material as a side product of powder production.

The oxide layer presented on the surface of metal powder particles breaks up during extrusion, leaving a fine dispersion of tenuous oxide network. Structures of this type were thoroughly investigated by light microscopy.²⁷) In addition, a deformation events decorated by oxide network were recorded during SEM observation of the extruded precursors²⁷,²⁸) the same as those shown in Fig. 3.

It is noticeable that oxide network acting as mechanical barrier strongly influences on the distribution of foaming agent particles, making them mostly fitted to banded structure formed in powder compacts after extrusion.

Despite of oxide particles are too small to be reliably captured by SEM, they can be clearly recognized by TEM observation of the precursor material, as shown in Fig. 4(a).

Radiation with characteristic wavelength attributed to oxygen is detected by EPMA measurements in spectrum of Al precursor, suggesting formation of Al₂O₃ oxide. In the sam-
ples produced from powder of ZAM alloy (Fig. 4(a)), the presence of magnesium besides aluminium and oxygen is found in spectrum, suggesting the formation of complex oxide (presumably MgAl$_2$O$_4$ spinel).

Attention should be paid to the fact that tenuous interconnected network of fine oxide particles is detected in the cell wall material of solid foam, as shown in Fig. 4(b). This fact indicates that nanometre-sized oxide remnants survive in the melt for a long time during foaming and, thus, remain in the cell wall material after solidification, as it was previously supposed.\(^{27}\)

Nevertheless, other micrometre-sized particles detected on the cell surface and in the cell wall material are rather different for studied kinds of foams. Foreign particles of partly converted TiH$_2$ rounded by Al$_3$Ti layers (A) and its reaction products such as Al$_3$Ti particles (B) as well as traces of (Al+Al$_3$Ti) eutectic domains (C) are randomly scattered in the cell wall material of hydride kind of Al-foams, as can be seen in Figs. 5 (a) and (b).

Some CaO/CaCO$_3$ particles (D) captured by Al$_3$O$_2$ oxide network (E) are revealed in the cell walls of carbonate kind of Al-foam, as can be seen in Fig. 5(c). This fact indicates that the oxide network captures powder particles of foaming agent in trap, leaving their products in the cell wall material after solidification.

However, cell wall microstructure of carbonate kind of ZAM alloy foam was found to be rather different.\(^{27}\) Particles of CaO/CaCO$_3$ (D) accumulate preferably within the eutectic domains of redundant phase (F) enriched by low-melt alloyed elements, as shown in Fig. 5(d). In particular, the results of EPMA analysis show that Mg content in redundant phase increases up to 20 mass%. As a result, micrometre-sized pores (G) lengthways eutectic domains (F) are generated by CO$_2$ gas. Non-wetted particles of CaO oxide being the product of decomposed CaCO$_3$ are predominantly located at the surface of these micrometer-sized pores, as can be seen in Fig. 5(d).

The next aspect concerns distinctive features of the cell face structure indicative of different foams. In hydride kind of Al-foam, some Al$_3$Ti particles (K) being the reaction products of partially converted TiH$_2$ (L) are randomly distributed in the cell face, as can be seen in Fig. 6(a). As opposed to this, numerous particles (M) corresponded to CaO and unconverted CaCO$_3$ are tight-fitted to the cell face of Al-foams created from carbonate bearing precursors, as shown in Fig. 6(b).

Furthermore, indications attributed to the presence of thin oxide skin on the surface of cell face and additional agglomeration of oxide particles in the cell wall were obtained by EDX analysis, as shown in Fig. 7(a). The reason of the above phenomenon is commonly ascribed to oxidation process originated from the decomposition of CaCO$_3$ foaming agent.\(^{7,8}\)

Figure 7(b) shows that radiation with characteristic wavelengths attributed to aluminium, oxygen, calcium, and carbon are detected in spectrum from the cell face surface, suggesting the formation of aluminium oxide (Al$_2$O$_3$) and Ca-bearing particles including those of calcium oxide (CaO), calcium carbonate (CaCO$_3$), and/or spinels (CaAl$_2$O$_7$, Ca$_3$Al$_2$O$_6$).

In addition, characteristic wavelength attributed to cooper is detected in spectrum from the cell face surface of carbonate kind of foam based on ZAM alloy, implying the formation of complex oxides (presumably Cu$_2$Al$_2$O$_4$). The results of EDX analysis specify that spectrum detected from material adjacent to CaO/CaCO$_3$ particles captured by the cell wall material is almost the same as that from the cell face surface. Unlike this, no indications of oxygen in the fresh cut surface of the cell wall material free from Ca-bearing particles were
obtained.

It is important to note that no accumulation of oxides at gas-metal interface of hydride kind of foams is detected in contradiction to assumption of Wübben et al.\textsuperscript{15) and Weigand.\textsuperscript{28)} Concerning cells morphology it was revealed that they are slightly elongated in the direction of extrusion and most samples are of similar porosity more than 80%. Carbonate kind of foams contains cells with mean size ranged from 1.1 to 1.2 mm while those for hydride foams varies in the range from 1.9 to 2.2 mm. Thus, mean cell size of carbonate kind of foams is found to be at least twice smaller as compared to that of hydride kind of foams.\textsuperscript{7,8)}

All the above results justify that the oxidation of Al melt by CO\textsubscript{2} gas leads to formation of oxide skin on the cell face surface as well as additional fraction volume occupied by Al\textsubscript{2}O\textsubscript{3} oxide network in the cell wall material of carbonate kind of foams.

3.3 Wetting behaviour of solids in contact with liquid Al

The results of immersion testing are listed in Table 2. These results indicate that both CaCO\textsubscript{3} and TiH\textsubscript{2} foaming agents are rather non-wetted by liquid Al. Moreover, wetting contact angle for CaCO\textsubscript{3} is greater than that for TiH\textsubscript{2}.

In line with known effect of surface roughness on the wetting results, contact angle for compacted tablet of CaCO\textsubscript{3} powder was found to be greater by 8° than that for the polished marble plate. However, contact angles determined by the sessile drop method are much smaller than that measured at immersion testing. It is known that wetting behaviour of a solid in contact with liquid metal is generally affected by not only thermodynamic characteristics such as reactivity and solubility but also by other external variables. Thus, the differences in wetting modes and atmosphere, which were used in immersion testing and sessile drop method, are the reasons of some discrepancy in the results. In addition, temperature achieved in sessile drop method is somewhat higher than that at immersion testing although holding time for both modes were the same. Generally, the results determined by sessile drop method confirm non-wetting mode for both kinds of foaming agents in liquid Al, as evidenced from Table 2.

As it is shown in Fig. 8, a contact angle measured for CaCO\textsubscript{3} by sessile drop method decreases to equilibrium value for holding time about 5 min and, then, stays unchanged. This suggests a very slow change of interface from Al/CaCO\textsubscript{3} to Al/CaO couple within the studied period although the results determined during isothermal TGA measurements of decomposition kinetics for CaCO\textsubscript{3} powder indicated the start of gas-release (mass loss) at the temperatures of interest.\textsuperscript{6,8)}

Nevertheless, only small events for transformation of Al/CaCO\textsubscript{3} system into Al/CaO are revealed by SEM observation of interface under drop which was removed from marble plate after holding time of 5 min at 750°C. As it can be seen Fig. 9(a), pronounced events of CaO oxide formation are de-
detected at the above said temperature after a holding time longer than 20 min whereas the presence of Al in marble surface under removed drop is not revealed by EDX analysis.

Of importance is the effect of alloying elements and, in particular Mg, on wetting behaviour of CaCO₃ in contact with ZAM-alloy. It is difficult to measure the contact angle of CaCO₃ with ZAM alloy due to Zn and Mg intensive evaporation in vacuum. Therefore, pure Al was firstly oversaturated by Mg up to 30% and then dropped onto marble plate. The wetting data listed in Table 2 show that unlike pure Al the synthetic Al-30Mg alloy wets the marble plate better. The presence of Mg on the interface after removing the drop from marble plate suggests the formation of complex CaOₓMgO oxide (MgAl₂O₄ spinel). The latter is formed at the temperature ranged from 650 to 700°C for the holding time about 5 min, as shown in Fig. 9(b).

By using the wetting data for Al-30Mg alloy it is easy to prove why particles of CaO/CaCO₃ accumulate predominantly in the domains of Mg-rich redundant phase presented in the cell wall material of carbonate kind of foam based on ZAM alloy.

As it is seen from Table 2, Al₃Ti is rather non-wetted by Al melt. Contact angle measured for Al₃Ti by sessile drop method decreases as holding time increases and, then, arrives stable equilibrium value (θ = 99°) at holding time about 10 min and longer, as can be seen in Fig. 8. Neutral wetting regime (θ = 90°) was found to be indicative of Al₂O₃ in contact with Al melt at 700°C in contradiction to the point of view postulated non-wetting regime for Al₂O₃ particles. Neutral wetting regime was determined at 700°C for alumina in contact with Al-7Cu alloy. Therefore, it could be resumed that doping Al melt by Cu in amount less than 7 mass% does not lead to a significant change in wetting behaviour of Al₂O₃ at 700°C. However, as applied to ZAM-alloy it is reasonable to point out that adding the alloying elements such as Mg and/or Zn to Al melt can, generally, change the wetting regime for Al₂O₃.

4. Discussion

Evidences of in situ experiments fulfilled in the present study indicate that application of CaCO₃ as alternative foaming agent results in remarkable improvement of foam stability the same as it was previously reported. On the first glance it could be thought that differences in foam expansion and stability are caused by differences in kinetics of TiH₂ and CaCO₃ decomposition. This aspect is especially important since blowing gas continuously escapes from the foam to the ambient atmosphere and counterbal-
anced by gas produced by the foaming agent. Indeed, TiH₂ is quickly exhausted at the temperature ranged from 600 to 700°C, whereas CaCO₃ decomposes continuously up to 850°C. Nevertheless, at the temperature slightly above melting point of aluminium (660°C) hydrogen gas releases from TiH₂ for about 10 min, which would be quite enough time to compensate the gas loss at the given experimental conditions. This fact allows us to resume that the reason for decay of hydride kind of foams is resulted by drainage and cell coalescence due to film rupture but not from the lack of H₂-gas.

It is commonly considered that solid inclusions hold the key for understanding of foam stability. The above subject matter is especially essential as to the foams fabricated via powder compact route since a lot of fine oxide particles entered in the melt as the side product. Great importance of oxide particles in foaming behaviour of powder precursor was previously pointed out. It was shown that amount of oxide particles is strongly dependent on the atmosphere of atomization process while optimised content of oxygen is usually accepted in the range from 0.1 to 0.4 mass%.

Generally, the main part of oxygen is assumed to form a thin oxide layer upon the surface of metal powder particles. In addition, some oxide content is sometime detected inside air-atomized powder particles. This is because of broken oxidized layer are presumably pulled into the liquid droplet by convection during atomization.

That is why the role of particles/layers in terms of their effect on stabilization of foams created from powder compacts should be mentioned here and discussed on the base of results obtained in the present study.

4.1 The role of oxide network particles in stabilization of foamy melt

First of all it is reasonable to note that stability of foams produced via powder compact route using both kinds of foaming agents is much higher than that indicative of other processes. In particular, foaming precursors can be carried out at higher temperature and increased dwell time compared to those used in melt processing like Alporas route. Distinctive feature of powder compact route is a huge number of nanometre-sized oxide particles, which are brought in melt by oxidized Al powder and formed in situ as side reaction products of foaming agents. The above difference becomes especially pronounced when oxide skin on the cell face surface was formed owing to application of CaCO₃ as foaming agent.

Following Babscan , classification regarding the type and size of solid inclusions seems to be helpful for understanding their role in stabilization of foams created via powder compact route. Network of nanometre-sized oxide remnants presented in the melt as a side product of powder metallurgy can be ascribed to gel-like colloidal system where as micrometer-sized particles of foaming agents and their side reaction products are indicative of suspension, which is not colloidal in a strict sense. The obtained results witness that the network of oxide remnants plays an important role for foam stability as it was originally pointed out by Körner et al. It was reported that hydrodynamic forces generated during foaming lead to a network fragmentation and clustering, and, finally, result in formation of tenuous super particles, which size is variable and dependent on the processing conditions. In order to explain the mechanism of foam stabilization due to the presence of oxide network super particles in-between the interfaces it was assumed that they are completely wetted by liquid aluminium and, therefore, sucked into the melt. In this consideration, contact angle about θₐ = 63° measured for Al/Al₂O₃ system at 1100°C was accepted as argumentation. It seems that the argumentation is somewhat a controversial since the contact angle accepted for validation of the above assumption was measured for Al/Al₂O₃ system at 1100°C whereas the temperature of 665°C was kept during foaming of precursor based on powder of AlSi11.5Mg0.5 alloy. Contact angle about θₐ = 86° measured at 665°C for AlSi11.5/Al₂O₃ system was reported. This result is in a good agreement with that determined in the present study. Neutral wetting regime (θₐ = 90°) for system Al/Al₂O₃ was detected at 700°C. By considering the above evidences it could be resumed that oxide network particles behave as if they were completely wet and move freely within aluminium melt as long as they are first of all in colloidal state. This is a reason that oxide network particles survive for a long time in the melt under gentle foaming during in situ gas evolving from internal source, providing for foam stability. It is important to note that the foam stability decreases substantially when oxide network is destroyed, e.g. either by agitation or by external gas injection.

The next aspect concerns the fact that oxide network affects mobility of non-wetted particles of the foaming agents and/or their reaction products. The results specified that these non-wetted particles are partly situated at the opposing liquid-gas interfaces whereas part of them present in the gap between interfaces, as shown in Figs. 5 and 6. In contradiction to Wübben et al., who assumed that solid particles could be dragged inwards during foam solidification, another reasonable explanation exists. Oxide network is thought to be able to hinder a part of non-wetted particles of the foaming agent and/or their reaction products in melt, leaving them in cell wall material after solidification, as can be seen in Fig. 5. During fragmentation and clustering of the oxide network, non-wetted particles can be captured in a trap, slowing down their free moving in liquid aluminium. Non-wetted particles are expelled from parts of the melt depleted or completely free from oxide network, resulting in their agglomeration at the gas-liquid interface. Actually, under attempts liquid aluminium foaming without oxides network, Al₃Ti particles did sediment in the melt modified by flux of fluoride salts, loosing their stabilizing ability.

Furthermore, oxides network is able to restrict bubble nucleation and growth to their regions, resulting in conservation of micrometer-sized pores within the cell wall material, as can be seen in Figs. 5 (b) and (d). In the cell walls of foams created from CaCO₃-bearing precursors, non-wetted particles of CaO oxide being the product of decomposed CaCO₃ are predominantly accumulated on the oxidized surface of these captured micrometer-sized pores created by released CO₂ gas, as shown in Fig. 5(d). However, non-wetted reaction products such as Al₃Ti particles and particles of partly converted TiH₂ rounded by Al₃Ti-layer are also found in the cell walls of hydride kinds of foams. Finally, agglomerations of
clustered nanometre-sized oxide particles combined with micrometre-sized particles of foaming agents and/or their reaction products form stable colloidal/suspension complexes.

4.2 Stabilizing effect of clustered oxide network/particles configurations

Mechanism of foam stability has continuously been discussed in literature taking into account the presence of solid inclusions in a melt. As applied to foam created via powder compact route foam stability is exclusively discussed within the context of increased content of oxide particles.

Several ways were reported in literature to explain the stabilizing effect of oxide network particles. It has been postulated that this oxide network holds the liquid in pockets with a very high effective viscosity, suggesting the delay of a drainage rate. However, it is difficult to explain foam stability only in terms of bulk viscosity. Furthermore, Wübben et al. found in micro-gravity experiments that the effect of solid inclusions on foam stability has primary to be ascribed to prevention of bubble coalescence while their effect on viscosity is of less importance. According to alternative point of view particle stabilization mechanism has been explained by mechanical stability of the oxide network particles infiltrated by liquid metal. Acting as effective mechanical barrier these network particles create long range repulsing force, the disjoining pressure, which prevent the cell wall thinning and rupture.

However, it is difficult to explain difference in stability of carbonate and hydride kind of foams only by mechanical stability of nanometre-sized particles of oxide network together with captured micrometre-sized particles.

Increased stability of aluminium foams created by CaCO$_3$ foaming agent is currently associated with additional stabilizing action of the cell face oxide skin which was formed via a reaction of liquid Al with oxidising CO$_2$ gas. Generally, the formation of oxide layer is considered to be primary responsible for efficient inhibition of cell coalescence and retention of fine cell structure.

The ways proposed to explain the role of oxide layer on cell face surface in terms of its effect on foam stability were summarised. In foams created from aluminium melt in form of suspension, oxide layer was thought to be able largely reduce the drainage by pushing the wetting particles of SiC into a liquid film, ultimately pinning them and preventing their moving upwards. According to alternative explanation, the oxide layer does not influence the drainage but it would primarily prevent the cell coalescence due to rupture of liquid films by damping the surface waves originated by mechanical or thermal perturbations. Despite of all attempts to explain the mechanism of stabilizing effect of the cell face oxide skin, it is still disputable.

In our opinion, improved stability of carbonate kinds of foams could be explained on the base of stabilizing models proposed by Kaptay in fundamental theoretical approach. These stabilizing models were developed in the assumption that a presence of clustered particles/network in melt leads to creation of interfacial force (disjoining pressure), separating the two opposing gas-liquid interfaces. In this approach, intervals of contact angles and several possible configurations of solid particles/network were specified as those mainly responsible for liquid foams stability.

Based on the present data and those reported it is easy to show that the cell wall microstructure of carbonate kind of foam is a very similar to configuration denoted as closely packed ‘double+’ layer of particles (CP2+) whereas distribution of particles/network for hydride kind of foam can be attributed to configuration denoted as loosely packed ‘double+’ layer of particles (LP2+C), see Fig. 10. Actually, the presence of clustered particles of oxide network together with captured particles situated between gas/liquid interfaces was believed to be a typical for both kinds of foams. The difference is that the opposing sides of cell faces for carbonate kind of foam are covered by oxide layers with embedded micrometre sized CaO/ CaCO$_3$ particles while those for hydride kind of foam comprises only free-standing Al$_3$Ti/TiH$_2$ particles.

Of importance is a fact that the ability of CP2+ configuration of solid particles to stabilise liquid foam is much superior to that of LP2+C one. CP2+ configuration of particles situated at the interfaces acts as ‘elastic separators’ of neighbouring cells. In addition, stabilizing contact angles meaningful for one or another configuration of solid particles were found to be rather different. CP2+ configuration can stabilise the liquid foam when contact angles lie in the interval 35$^\circ$ < $\theta$ < 180$^\circ$, although the optimum value of contact angle is about $\theta$ = 89$^\circ$. Stabilizing effect of LP2+C configuration reveal itself in the interval 20$^\circ$ < $\theta$ < 129$^\circ$ while optimum contact angles vary in the range from 72$^\circ$ to 88.5$^\circ$.

The wetting data determined in the present study (Table 2) indicate that contact angles for all types of solid inclusions with liquid Al/ZAM alloy meet the stabilizing conditions prescribed by both configurations. Moreover, stabilizing contact angle determined for Al$_2$O$_3$ at the temperature of interest is nearly the optimum value.

Thus, a formation of solid oxide layers on the opposing cell surface decorated by embedded oxide particles, which are linked by bridges of oxide network/particles, act the most effective against the cell coalescence, providing the high foam stability. Indeed, the particles of foaming agents and/or their reaction products can also serve as foam-stabilisers to some extent, although their effect on foam stability is of less impor-

![Fig. 10 Schematic presentation of the cell wall structure of (a) carbonate and (b) hydride kind of foams (adopted over experimental observation) as compared with (c), (d) configurations of stabilising particles (adopted over Ref. 25)): (c) closely packed double+ layer of particles (CP2+); (d) loosely packed double+ layer of particles (LP2+C). In (a) micrometre-sized pore (black) and micrometre-sized particles of CaCO$_3$ (grey)/CaO (white), which are either captured by network of nanometre-sized oxide particles or embedded in the oxidised surface of the cell face; in (b) micrometre-sized pore (black) and micrometre-sized particles of Al$_3$Ti (grey)/TiH$_2$ (white) rounded by Al$_3$Ti layer, which are either captured by network of nanometre-sized oxide particles.](image-url)
tance.

As an important remark it should be pointed out that one might speculate that models, proposed by Kaptay are not realistic because particles are not connected as it was prescribed by models. The researches thought that the disjoining force should be transmitted mechanically via this dense particle packing. However, Kaptay notified in advance that Equations derived for loosely packed network of clustered particles (an LPNC-structure) are in the first approximation the same as for the more ‘regular’ structures (e.g. LP2C and LP2+C). Moreover, as it was suggested by Kaptay loosely packed clustered particles or even their network (LPNC) are mainly responsible for the stabilisation of liquid foams in majority of cases.

5. Conclusions

Foam formation at heating of powdered compacts based on Al/AlZnMg alloy has been studied in course of in situ experiments using X-ray apparatus. Several kinds of precursors comprising a conventional titanium hydride (2 mass% TiH2), calcium carbonate (2 mass% CaCO3) and/or mixture of foaming agents (1.5 mass% TiH2+0.5 mass% CaCO3) have been used.

Three meaningful periods, i.e. solid, semisolid, and liquid state of precursor, have been revealed during heating of precursors up to 700°C. It was identified that application of calcium carbonate provides with considerable improvement of foam expansion and stability as compared to titanium hydride.

By considering stabilizing action of particles on foamy melt, evidences concerning characteristic features of cell wall material and relevant wetting data have been determined to elucidate the difference in stability of carbonate and hydride kind of foams.

Several kinds of foreign inclusions contained by cell wall material have been recognized and classified. It was shown that the network of nanometre-sized oxide particles brought in the melt as a side product of powder metallurgy remains in the cell wall structure after foam solidification. Oxide particles survive in the melt as long as they are in colloidal state since they have very small size and Al2O3 oxide shows neutral wetting (θw = 90°) by liquid Al at 700°C.

Micrometer-sized particles of non-wetted foaming agents and their reaction products (either particles of CaO/CaCO3 or Al3Ti and Ti-rich particles rounded by Al3Ti layer) are mainly agglomerated at the cell face surface although some of them were found within cell wall material. A majority of non-wetted particles are basically expelled from melt depleted or completely free from oxide network. In another way, oxide network captures some part of non-wetted particles in a trap, slowing down their free moving in melt. As a result, clustered nanometre-sized oxide particles combined with micrometer-sized particles of foaming agents and/or their reaction products form stable colloidal/suspension complexes.

In the instance of carbonate kind of foam based on AlZnMg alloy, agglomeration of clustered network/CaO particles were found within eutectic domains contained by the cell wall material since CaCO3 particles get completely sucked into redundant phase as long as they are well wetted by melt enriched by Mg. Moreover, oxide network of complex oxides (presumably, MgAl2O4 spinel) being formed owing to CO2-gas/melt reaction restricts bubble nucleation and growth to their regions, resulting in conservation of micrometer-sized pores within the domains of redundant phase.

It was specified that the oxidation of melt by CO2 gas results in pronounced difference of cellular structure for carbonate and hydride kind of foams. The main characteristic of carbonate kind of foams concerns the formation of oxide skin on cell face surface and increased fraction volume occupied by clustered nanometre-sized oxide particles as well. Thus, a distribution of solid inclusions in cell walls of carbonate and hydride kind of foams was found to be different. Opposing cell faces of carbonate kind of foams are covered by an oxide skins with embedded non-wetted CaO/CaCO3 particles whereas those of hydride kind of foams contain free-standing particles of non-wetted foaming agent and its reaction products, i.e. Al3Ti and partly converted TiH2 particles rounded by Al3Ti layer.

The results of this effort proved that that stabilizing models given by Kaptay for a variety of solid particles configurations can be used as a guideline to explain the difference in evolution and stability of carbonate and hydride kind of foams. In framework of this stabilization theory, foam stability is explained by assuming interfacial force, the disjoining pressure, which efficiency is variable and dependent on the configuration and wetting behaviour of clustered particles/network in the melt.

It was recognized that the distribution of solid inclusions in the cell wall of carbonate kind of foam is a very similar to configuration denoted as closely packed ‘double+’ layer of particles (CP2+) whereas distribution of particles/network for hydride kind of foam can be attributed to configuration denoted as loosely packed ‘double+’ layer of particles (LP2+C). Wetting data determined in the present study indicate that contact angles for all types of solid inclusions are in a good agreement with those prescribed by the theory as stabilizing values for each of proper configuration, i.e. CP2+ and LP2+C. If so, the improved stability of carbonate kind of foam compared to hydride one can be explained within framework of the above said stabilization theory. In accordance with theoretical models, stabilizing effect of configuration (CP2+) is much superior to that of configuration (LP2+C).

The obtained results bring to a better understanding of particle stabilizing mechanism operating a lot of foaming processes.

Acknowledgements

This research was supported by National Academy of Science of Ukraine under the Project No III-2-13. Special thanks to the researchers of Tohoku University, Japan, for fruitful discussions and cooperation.

REFERENCES