Grain Refiners as Liquid Metal Foam Stabilisers

N. Babcsán1,2, G.S. Vinod Kumar1,3, B.S. Murty4 and J. Banhart1,2
1Hahn-Meitner Institute, Berlin, Germany
2Technical University Berlin, Germany
3NFTDC, Hyderabad, India
4Indian Institute of Technology Madras, Chennai, India
E-mail: babcsan@hmi.de
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ABSTRACT
The present work reports on the foaming of liquid aluminium containing TiB2, TiC or TiAl3 particles (4-11.5 vol.%) which were prepared in-situ by flux-assisted melting using fluorides. This procedure was in analogy to the production of composites containing grain refining particles. The particle size was kept below 1 µm for TiB2 and TiC and around 10 µm for TiAl3. Foams were successfully produced using TiB2 and TiC particles and thus it could be demonstrated for the first time that metal foams can be stabilised by sub-micrometre particles. The influence on foam stability of alloying with Si and dilution of the melt with pure Al was studied in addition. Microstructural analysis of the foams showed that the particles segregate to the surfaces of cell walls leading to an almost dense coverage, thus helping in stabilising the foams.

1. INTRODUCTION
Metal foams belong to the class of cellular materials which are the basic structural materials of nature. Replacement of the weak natural matrix (e.g. wood) by a stronger metal leads to a stronger artificial material which has already a great potential in the car and building industries. Among the metals aluminium alloys have the best prospects. Production of metal foams requires stabilizing particles which can be either nanometre-sized oxide filaments or micrometer-sized particles. The size and type of particles have a pronounced impact on mechanical properties. When micrometre-sized particle are present the foams are more brittle and cutting is difficult. Sub-micrometre particles lead to more favourable mechanical properties and less problems with machinability. Particle size and shape divide the production routes into two classes: nanometre-thick filaments are used whenever an internal gas source is exploited for pore generation, i.e. a blowing agent, whereas micrometre-sized particles are suitable when gas is blown into the melt from an external source via an injector. There is another important difference: filaments form networks which remain in the bulk of the foam films whereas micrometer-sized particles segregate at the metal/gas interfaces. Using smaller particles the particle volume fraction required to cover surfaces to a given degree can be reduced, thus implying both better cost efficiency and mechanical properties.

It remains to analyse the methods available to introduce or produce sub-micrometre or even nanometre-sized particles in liquid aluminium and to see if such composites with ultrafine particles are foamlable. Mixing of very small particles into liquid aluminium is obviously very difficult. Mixing and compaction of aluminium powder and stabiliser powder is a possibility but involves the oxide skins on the Al powder particles which possibly cause detrimental effects. In-situ reactions triggered within a aluminium alloy melt can produce good quality precursors as it is done in case of Alporas foams by oxidation of the melt. On the other hand, sub-micrometre-sized carbide and boride particles are already used in master alloys containing grain refiners. Hence, the flux assisted melting method which is applied for commercial grain refiner production could be a good candidate for being used for making foamlable precursors containing ultrafine particle.

The essential properties of the stabilising particles which lead to foamlability are still a subject of debate. One can argue that the contact angle between particles and melt is the key issue. Good summary of the experimental results of the foamlability dependence on contact angle is listed in Ref. 1. Kaptay derived a stability range of 60-90°. Babcsán et al. have shown that particles segregating to the surface of a metal foam film lead to a foam, whereas melts containing non-segregating particles or particle free alloys cannot be foamed. The necessity of segregation for stability, even more evidently, has been shown in ceramic particle stabilised aqueous foams. A high quality foam has equally sized bubbles, smooth cell walls and lacks of bulk liquid on the bottom of the sample.

2. EXPERIMENTAL DETAILS
The foamlable precursors consist of aluminium alloys containing 6 vol.% TiB2, 4 vol.% TiC or 11.5 vol.% TiAl3, which are prepared by flux-assisted melting using fluoride salts. Particle size was kept below 1 µm in case of TiB2 and TiC and around 10 µm in case of TiAl3. The purity of the aluminium was 99.85%. All the materials were produced in a graphite crucible at 800 °C (Al-TiB2) or 1200°C (Al-TiC).

Foams were made in Al2O3 crucibles by mixing 1.6 wt.% of TiH2 blowing agent into 30-60g melted precursor at 700°C while vigorously stirring at 900 rpm for 100s. After mixing, the foam was isothermally held for up to 200 s which roughly corresponds to maximum expansion according to the literature. As a first attempt, conditioned TiH2 powder
(pre-oxidised in air for 3 h at 480°C) was used which is a usual procedure in making powder metallurgical foams \(^\text{11}\) and the Formgrip foam making process \(^\text{12}\). The second attempt was to use untreated TiH\(_2\) which is generally used in making Alporas-type foams \(^\text{13}\). The temperature of foaming also significantly influences the hydrogen flux and hence the evolution of the foam has to be chosen carefully \(^\text{14}\). Experimental parameters of the various foaming experiments are shown in Table 1. Foam macrostructure was characterised by X-ray radioscopy using a micro focus X-ray source and a panel detector as described elsewhere \(^\text{15}\) and by photographing the metal foam cross cuts. For microstructural characterisation samples were cut and polished with SiC paper followed by polishing with a diamond suspension.

### 3. RESULTS

Blowing pure Al with TiH\(_2\) did not lead to foam as is evident from Fig. 1(a), although some bubble residues remained on the top of the sample. The Al-TiAl\(_3\) composite could also not be successfully foamed as shown in Fig. 1(b). In contrast, the Al-TiB\(_2\) composite melt could be used as a useful precursor for foam as is observed from Fig. 1(c). Al-TiB\(_2\) composites led to even better foams with more cells and less drainage (Fig. 2(a)). Fig. 2(b) indicates that untreated TiH\(_2\) causes a higher expansion. Diluting the TiB\(_2\) containing composite with pure aluminium has reduced the amount of the foam as is evident from Fig. 3(a) and (b). Significant drainage was observed after aluminium addition (Fig. 3(b)), but pores are smaller and more regular. Diluting the TiC containing composite with pure aluminium has produced the similar detrimental effect as for Al-TiB\(_2\) composites, see Fig. 4(a) and (b). TiAl\(_3\) addition to TiC composite did not affect significantly the amount of the foam (Fig. 4(c)), while the addition of some silicon to the TiB\(_2\) composite had a strong negative effect on foaming (Fig. 4(d)).

A microstructural analysis of the foams indicates that TiAl\(_3\) particles were not able to attach to the surface of the bubbles as is evident from Fig. 5(a) and most of the particles settled down to the bottom of the melt, Fig. 5(b).

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## Table 1

Experimental details of the foaming experiments

<table>
<thead>
<tr>
<th>No.</th>
<th>Matrix composition</th>
<th>Particle type</th>
<th>Particle content, vol. %</th>
<th>Holding time, s</th>
<th>TiH(_2) particle type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Al none</td>
<td>0</td>
<td>50</td>
<td>Treated</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Al TiB(_2)</td>
<td>6</td>
<td>50</td>
<td>Treated</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Al TiAl(_3)</td>
<td>11.5</td>
<td>50</td>
<td>Treated</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Al TiC</td>
<td>4</td>
<td>50</td>
<td>Treated</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>Al TiC</td>
<td>4</td>
<td>50</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Al TiC</td>
<td>2</td>
<td>50</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Al TiB(_2)</td>
<td>6</td>
<td>50</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>Al-3.3 wt% Si TiB(_2)</td>
<td>4</td>
<td>50</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>Al TiC + TiAl(_3)</td>
<td>2, 5.75</td>
<td>50</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>Al TiB(_2)</td>
<td>6</td>
<td>200</td>
<td>Untreated</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>Al TiB(_2)</td>
<td>2</td>
<td>200</td>
<td>Untreated</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 2: Al-TiC composite foams with (a) treated (#4) and (b) untreated (#5) TiH$_2$ with 50s holding. Bottom of the sample is 30mm wide.

Fig. 3: Al-TiB$_2$ composite foam after 200s holding (a) without Al dilution (6 vol.% of TiB$_2$ particles, (#10) and (b) with Al dilution to 2 vol.% TiB$_2$ (#11), untreated TiH$_2$.

The present results indicate that the best foams are obtained when the particles are able to segregate to the bubble surface and decorate the surface so as to stabilise it and to prevent the film from rupturing.

The attempts to foam pure Al were not successful, which strengthens the idea that particles are necessary to stabilise liquid metal foams. The present results also indicate that TiH$_2$ particles, which are the source of hydrogen leading to bubble formation can also act as stabilisers to some extent. A similar result was reported for AlMg$_20$ alloys with 10 wt% TiH$_2$ addition. We observed TiH$_2$ particles at some cell wall surfaces which hydrides particles were intact. If the TiAl$_3$ particles were in the size range of 10-20 μm. SiC particles are used exactly in this size range to stabilise Metcomb-type foams although larger particles (70 μm) did.

4. DISCUSSION

The above results indicate that the use of TiB$_2$ and TiC particles improve foamability of aluminium. Among the three particles compositions studied, TiC appears to be the best in improving foamability. It is also interesting to note that while all the above particles induce grain refinement in Al and Al alloys, TiC appears to be the best as is evident from the previous studies of the authors. Thus it is likely to have some relationship between the ability of a particle to refine grains during solidification and to improve foamability. The ability of a particle to act as a good nucleating site to Al crystallisation depends on a number of parameters such as its crystal structure, number of available crystallographic planes that can act as substrates for nucleation, faceted nature of particle, its ability to wet the liquid Al, etc. The present results indicate that the best foams are obtained when the particles are able to segregate to the bubble surface and decorate the surface so as to stabilise it and to prevent the film from rupturing.

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Fig. 4: X-ray radioscopic images of foams made with (a) Al-4 vol.% TiC composite (#5), (b) Al-2 vol.% TiC composite (#6), (c) Al-2 vol.% TiC + 5.75 vol.% TiAl\(_3\) (#9) composite and (d) Al-3.3Si-4 vol.% TiB\(_2\) composite (#8). Bottom of the sample is 30mm wide.

Fig. 5: Optical micrographs of Al-TiAl\(_3\) foams (#3) showing, (a) TiAl\(_3\) particles away from the surface and (b) TiAl\(_3\) particles at the bottom of the foam.

not lead to stable foams in the Formgrip process. If the particles are too large, i.e. larger than the cell wall thickness, the particle will no longer act as a foam stabiliser. If the particle size is one magnitude smaller than the cell wall thickness the effect of the surface segregation can also be observed more evidently.

Data on wettability of TiAl\(_3\) with Al is not available, while Kaptay has reported the contact angle of TiB\(_2\) and TiC with Al in vacuum at 1100°C as 0 and 10°, respectively. Though the conditions of foaming in the present study are different from the above conditions, one can get a rough idea of the wettability of the two particles from the above report. The structure of TiAl\(_3\) being tetragonal, therefore TiAl\(_3\) is known to be not a very good grain refiner for Al in comparison to TiB\(_2\) and TiC. In addition, TiAl\(_3\) particles are bigger than the other two and do not act as a good stabiliser of foam. Contrary SiC particles having similar sizes are good foam stabilizers. They have a contact angle of 60° in Al-Si alloys which is in the range of contact angles that results good stability. Likely the inability of TiAl\(_3\) to segregate to the bubble surface is due to the wetting of the particles and not because of the larger size. Though TiB\(_2\) has...
Fig. 6 : SEM images of Al-TiB₂ foam showing (a) early pore, (b) TiB₂ particles at the cell wall and interdendritic regions and (c) Ti mapping of (b) image.

Fig. 7 : Images of Al- TiC foam showing (a) cell structure, (b) TiC particles at the cell wall, (c) enlarged view of the cell wall decorated with TiC particles and (d) sub-micrometre size range of TiC particles on the cell wall surface. Optical microscopy (a) SEM images (b,c,d).
0° contact angle (in vacuum at 1100°C), the particles being finer get segregated to the cell wall surfaces, while significant amounts of particles have also been observed in the matrix. TiC has a higher contact angle than TiB₂. Accordingly, it has a stronger surface activity and thus gets segregated to the bubble resulting in its stabilisation. Coarsening and larger drainage is the sign of the less stable system which can indicate the difference between the foam quality of TiB₂ and TiC containing foams. The presence of Si in AlSi₃.₃-TiB₂ composite has lead to poor foam in this study (Fig. 4(d)).

This result is in a good agreement with our previous work where we tried to foam AlSi₁₀-TiB₂ composite by gas injection at 700°C where only irregular bubble remnants could be produced moreover the TiB₂ particles fall out from the bubble surfaces leaving a significant amount of powder on the surface of the melt ¹⁷. Si is known to have a poisoning effect on the grain refinement efficiency of TiB₂ by reacting with it and forming titanium silicides on the surface of the TiB₂ particles and thus making them less potent nucleating sites for Al ⁴. A similar poisoning effect appears to work in case of foaming of TiB₂ containing aluminium melt, which leads to decrease stabilising ability of the particles due to the modified surface of the particles. Likely the different particle surface results different wettability which is finally decrease the foamability of the particles ¹⁸.

Liquid foams by definition are collections of gas bubbles dispersed in a continuous liquid phase or on the surface of a liquid. All stabilisers used in liquid foams can be included into the following categories: nucleation stabilisers, drainage stabilisers, and adsorption stabilisers ¹⁹. A nucleation stabiliser is a material that encourages gas bubble formation. Coarse-grained nucleation stabilisers are materials that act as a bubble nucleation site due to agglomerated or particle can be used for both jobs, for metal foams due to their stability is influenced by the addition of alloying elements.

(c) Ex-situ characterisation of the foams by SEM showed that both TiB₂ and TiC particles segregate to the surface of the cell walls leading to an almost dense coverage.

(d) It has been demonstrated for the first time that metal foams can be stabilised by sub-micrometre particles and that their stability is influenced by the addition of alloying elements.

(e) By using smaller amounts and sizes of particles than those present in the commercial Duralcan MMCs, the machinability of the end product will be improved significantly. Moreover, a cost advantage over Duralcan MMCs seems possible.

5. SUMMARY

(a) Aluminium foams were successfully produced using precursors made by flux-assisted melting using fluorides.

(b) TiB₂ and TiC particles proved to be good foam stabilisers, whereas TiAl₃ did not lead to any foam although the particles remained in the precursor.

(c) Ex-situ characterisation of the foams by SEM showed that both TiB₂ and TiC particles segregate to the surface of the cell walls leading to an almost dense coverage.

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