

Grain Refiners as Liquid Metal Foam Stabilisers

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(Received 30 June 2006 ; in revised form 20 November 2006)

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 particles¹. The size and type of particles have a pronounced impact on mechanical properties². Whenever micrometre-sized particles 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 while 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 foamable. 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 melt³. On the other hand, sub-micrometre-sized carbide and boride particles are already used in master alloys containing grain refiners⁴. Hence, the flux assisted melting method which is applied for commercial grain refiner production could be a good candidate for being used for making foamable precursors containing ultrafine particle.

The essential properties of the stabilising particles which lead to foamability 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 foamability dependence on contact angle is listed in Ref. 1. Kaptay derived a stability range of 60-90°⁵. Babcsán et al.⁶ 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^{7,8}. 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 foamable precursors consist of aluminium alloys containing 6 vol.% TiB₂, 4 vol.% TiC or 11.5 vol.% TiAl₃ particles, 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 (Al-TiB₂ and Al-TiAl₃) or 1200°C (Al-TiC)⁹.

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 literature¹⁰. As a first attempt, conditioned TiH₂ powder

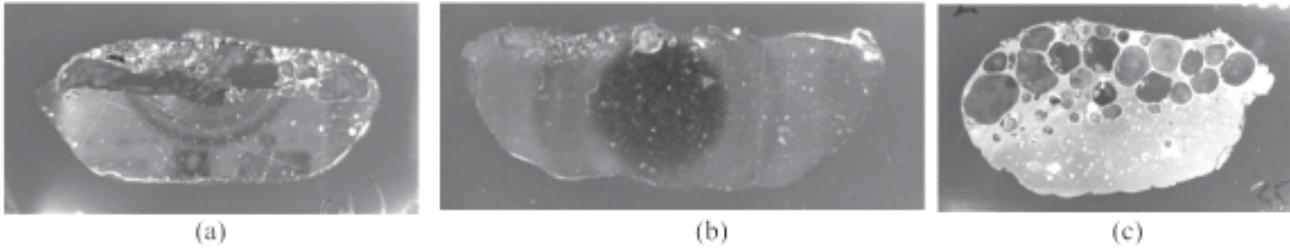


Fig. 1 : Samples foamed with treated TiH_2 with 50s holding, (a) Pure Al (#1), (b) Al-TiAl₃ composite (#3) and (c) Al-TiB₂ composite (#2). Blowing agent treated, no.'s refer to Tab. 1. Bottom of the sample is 30mm wide.

(pre-oxidised in air for 3^h at 480°C) was used which is a usual procedure in making powder metallurgical foams¹¹ and the Formgrip foam making process¹². The second attempt was to use untreated TiH_2 which is generally used in making Alporas-type foams¹³. The temperature of foaming also significantly influences the hydrogen flux and hence the evolution of the foam has to be chosen carefully¹⁴. Experimental parameters of the various foaming experiments are shown in Table 1. Foam macrostructure was characterised by X-ray radiography using a micro focus X-ray source and a panel detector as described elsewhere¹⁵ 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-TiAl₃ composite could also not be successfully foamed as shown in Fig. 1(b). In contrast, the Al-TiB₂ composite melt could be used as a useful precursor for foam as is observed from Fig. 1(c). Al-TiC 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 TiB₂ 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-TiB₂ composites, see Fig. 4(a) and (b). TiAl₃ addition to TiC composite did not affect significantly the amount of the foam (Fig. 4(c)), while the addition of some silicon to the TiB₂ composite had a strong negative effect on foaming (Fig. 4(d)).

A microstructural analysis of the foams indicates that TiAl₃ 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).

Scanning electron microscopy of foam containing TiB₂ particles showed aluminium dendrites and interdendritic regions filled with TiB₂ particles as shown in Fig. 6(a) and (b). At the beginning of pore formation the surface is partly covered but as the pore grows to a large bubble, the TiB₂ particles cover the whole surface of the bubble. The Ti mapping of the sample in Fig. 6(c) confirms the presence of TiB₂ particles both on the surface of the bubble and in the interdendritic regions. TiC stabilised foams exhibit straight cell walls and equally sized plateau borders as shown in Fig. 7(a) and (b). The average cell wall thickness of the foams is around 70 μm. Only few TiC particles can be found inside the cell walls and the particles are not interconnected

Table 1
Experimental details of the foaming experiments

No.	Matrix composition	Particle type	Particle content, vol. %	Holding time, s	TiH ₂ particle type
1	Al	none	0	50	Treated
2	Al	TiB ₂	6	50	Treated
3	Al	TiAl ₃	11.5	50	Treated
4	Al	TiC	4	50	Treated
5	Al	TiC	4	50	Untreated
6	Al	TiC	2	50	Untreated
7	Al	TiB ₂	6	50	Untreated
8	Al-3.3 wt% Si	TiB ₂	4	50	Untreated
9	Al	TiC + TiAl ₃	2, 5.75	50	Untreated
10	Al	TiB ₂	6	200	Untreated
11	Al	TiB ₂	2	200	Untreated

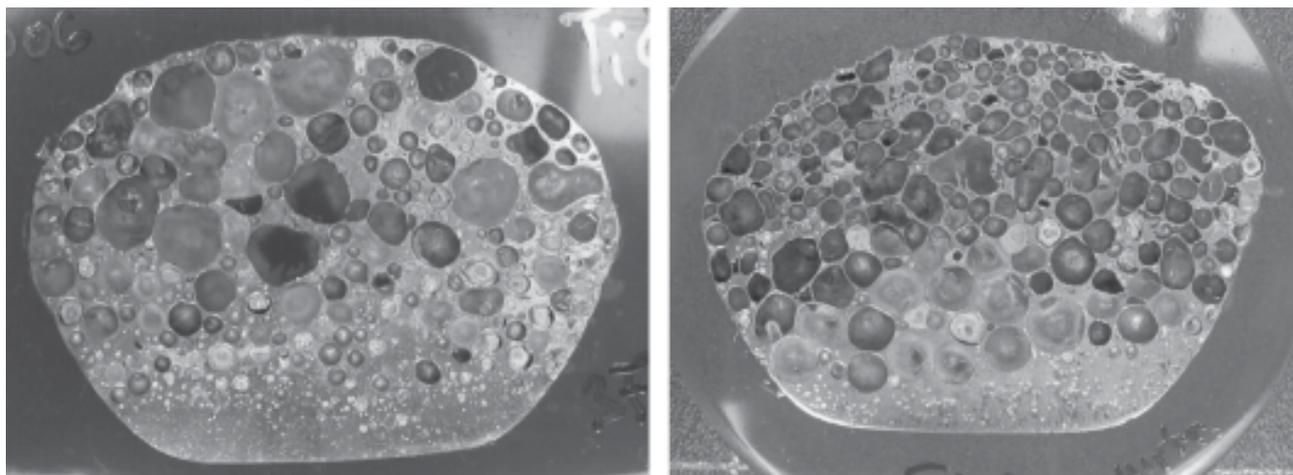


Fig. 2 : Al-TiC composite foams with (a) treated (#4) and (b) untreated (#5) TiH_2 with 50s holding. Bottom of the sample is 30mm wide.

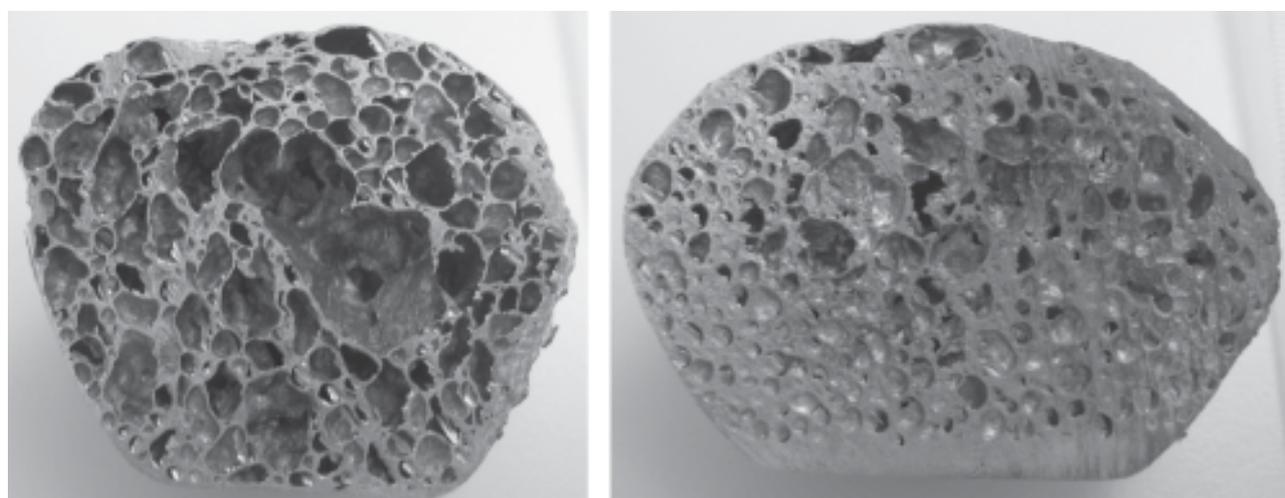


Fig. 3 : Al- TiB_2 composite foam after 200s holding (a) without Al dilution (6 vol.% of TiB_2 particles, (#10) and (b) with Al dilution to 2 vol.% TiB_2 (#11), untreated TiH_2 .

(Fig. 7(b)). The surface of the cell wall is densely covered with them (Fig.7 (b) and (c)). The distinguishable TiC particles have sub-micrometre dimensions as demonstrated by Fig. 7(d).

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 authors⁹. 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.⁴. 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 foams¹. 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 AlMg20 alloys with 10 wt% TiH_2 addition¹⁹. We observed TiH_2 particles at some cell wall surfaces which hydrides particles were intact. If the TiH_2 were able to incorporate into the melt a TiAl_3 layer was observed on the surface of these particles which is caused by the reaction of Ti formed after dissociation of TiH_2 and Al.

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 foams²⁰ although larger particles (70 μm) did

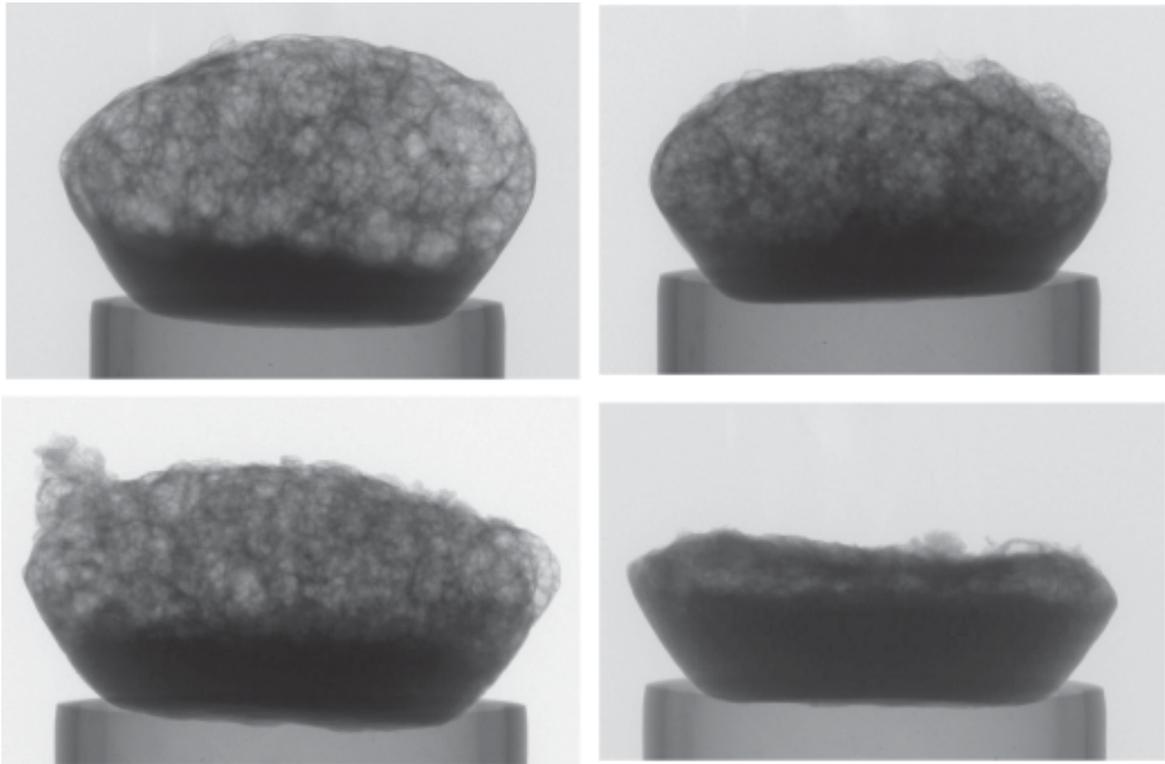


Fig. 4 : X-ray radioscopic images of foams made with (a) Al-4 vol.% TiC composite (#5), (b) Al-2 vol.% TiC composite (#6), (c) Al-2 vol.% TiC + 5.75 vol.% TiAl₃ (#9) composite and (d) Al-3.3Si- 4 vol.% TiB₂ composite (#8). Bottom of the sample is 30mm wide.

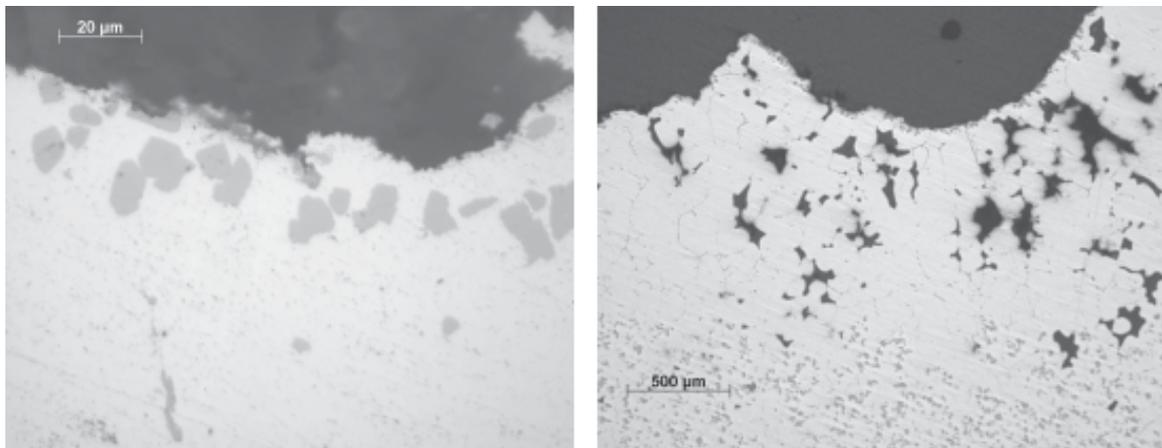


Fig. 5 : Optical micrographs of Al-TiAl₃ foams (#3) showing, (a) TiAl₃ particles away from the surface and (b) TiAl₃ particles at the bottom of the foam.

not lead to stable foams in the Formgrip process¹⁷. 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 TiAl₃ with Al is not available, while Kaptay¹⁶ has reported the contact angle of TiB₂ 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 TiAl₃ being tetragonal, therefore TiAl₃ is known to be not a very good grain refiner for Al in comparison to TiB₂ and TiC. In addition, TiAl₃ 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 stabilizers¹⁷. They have a contact angle of 60° in Al-Si alloys which is in the range of contact angles that results good stability¹. Likely the inability of TiAl₃ to segregate to the bubble surface is due to the wetting of the particles and not because of the larger size. Though TiB₂ has

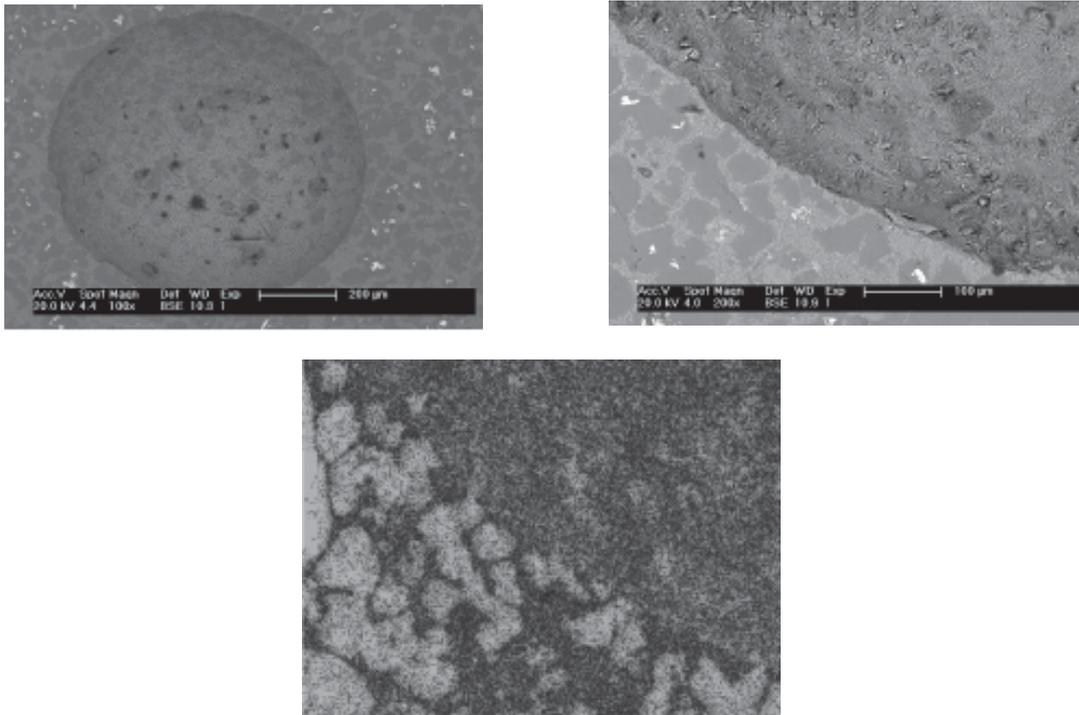


Fig. 6 : SEM images of Al-TiB₂ foam showing (a) early pore, (b) TiB₂ particles at the cell wall and interdendritic regions and (c) Ti mapping of (b) image.

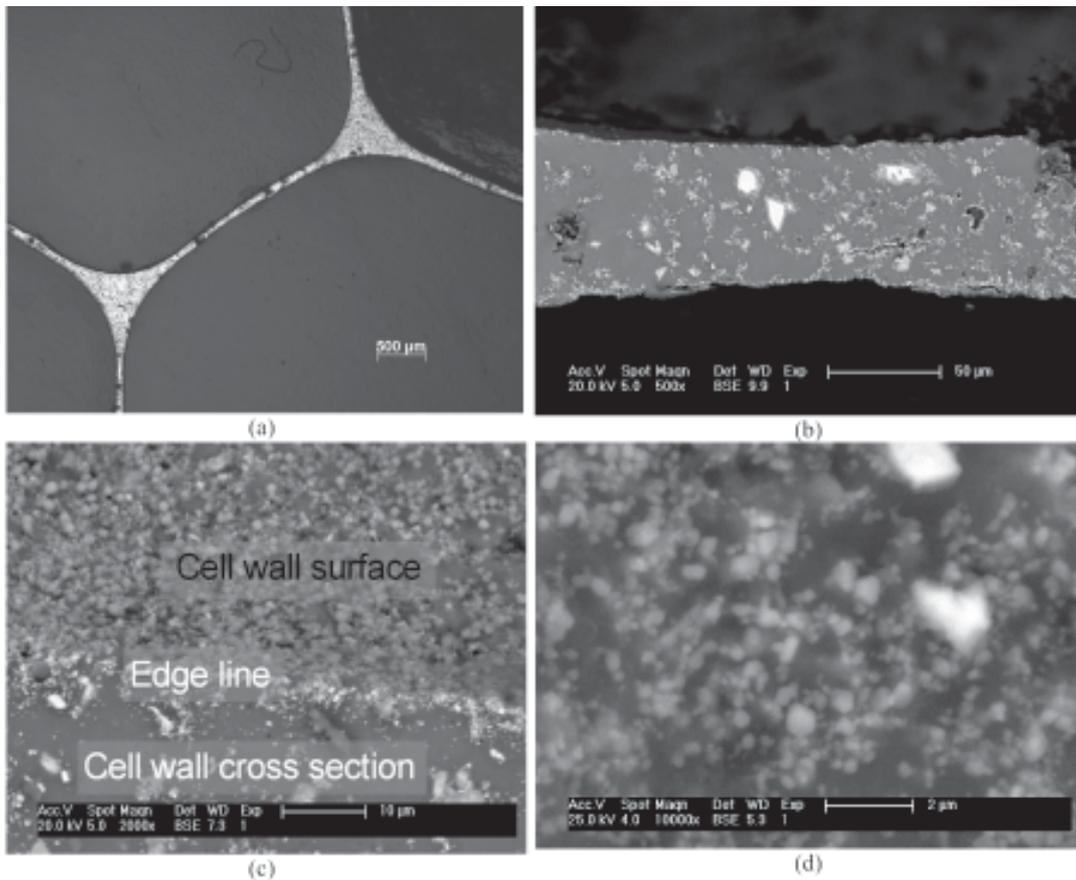


Fig. 7 : Images of Al-TiC foam showing (a) cell structure, (b) TiC particles at the cell wall, (c) enlarged view of the cell wall decorated with TiC particles and (d) sub-micrometre size range of TiC particles on the cell wall surface. Optical microscopy (a) SEM images (b,c,d).

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 led 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 melt¹⁷. 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 Al⁴. 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 particles¹⁸.

Liquid foams by definition are collections of gas bubbles uniformly dispersed in fluids and separated from each other by self-standing thin films¹. The basic difference between grain refiners and foam stabilisers are that grain refiners nucleate grains while foam stabilizers do not nucleate bubbles but stabilizes the thin liquid films via segregation on bubble surfaces. If the growing bubbles meet each other and it is not stabilised will rupture. In our case this rupture is prohibited by the grain refiner particles. Although the same composite or particle can be used for both jobs, for metal foams due to the large surface, significantly more particles are required. The bubbles likely are growing from preexisting pores produced during mixing the TiH₂ with the melt. If the particles would act as bubble nucleation site due to agglomerated particles one would see segregated particles on early pore surfaces of the foam which is not the case (Fig. 6a). The relationship between refiners and stabilisers is the wettability of particles. Both needs low contact angle to be effective. It has been found out that good grain refiner are also good foam stabiliser. Although detailed pictures of the similarities cannot be drawn in this paper.

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.

- (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.

ACKNOWLEDGEMENT

The authors would like to thank Miklós Korniyik and Zsuzsa Filep for microstructural characterisation. Support by DFG and INSA for a travel grant for one of the authors (BSM) is gratefully acknowledged.

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