New Foam Stabilizing Additive for Aluminium

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ABSTRACT

Liquid metals are mostly made foamable by Ca additions followed by a thickening period. There is a need for an additive that can be easily admixed to an aluminium alloy melt and makes this melt foamable. We have selected aluminium-based grain refiner composites to test their foamability. TiB_2, TiC or $TiAl_3$ particles were produced in the melt by flux-assisted melting using fluoride salts. The particle size was kept below 1 μm for TiB_2 and TiC and around 10 μm for $TiAl_3$. The composites were heated to above their melting point (700°C) and were then foamed by either the addition of TiH_2 or by injecting gases into the melt directly.

Foams were successfully produced using TiB_2 and TiC particles, while $TiAl_3$ did not lead to any foam. Foam stability increased from TiB_2 to TiC. Ex-situ characterisation of the foams by SEM showed that the particles segregate to the surfaces of the cell walls and lead to almost dense coverages there. Even after dilution of the initial composite a significant amount of foam can be still produced, indicating that these composites are suitable foam stabilizing additive for aluminium alloys and that foams based on small volume fractions of non-metallic additives can be produced.

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 an improved artificial material which is already finding application in the car and building industries. Among the different 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 [1]. The size and type of particles have a pronounced impact on mechanical properties [2]. Whenever micrometre-sized particle are present, the foams are more brittle and cutting is difficult. Sub-micrometre particles should lead to more favourable mechanical properties and less problems with machinability.

The current task is to analyse the methods available for incorporating sub-micrometre or even nanometre-sized particles into liquid aluminium and to verify that such composites are foamable. Admixing very small particles to liquid aluminium is obviously very difficult. Mixing and compaction of aluminium powder and stabiliser powder is a possibility but relies on more expensive powders. By adding compacted powders to melts during ultrasonic melt treatment good foams were produced [3] as the powders contain stabilizing oxides, but in this work we selected another way: In-situ reactions triggered within an aluminium alloy melt can produce good quality precursors as it is done in case of Alporas foams by oxidation of the melt [4]. On the other hand, sub-micrometre-sized carbide and boride particles are already used in master alloys containing grain refiners [5]. Hence, the flux assisted melting method which is applied for commercial grain refiner production could be a good candidate for being used to manufacture foamable precursor for aluminium melt and will be studied in the following.

EXPERIMENTAL

The composites consist of aluminium alloys containing either 6 vol.% TiB_2, 4 vol.% TiC or 11.5 vol.% $TiAl_3$

particles and were prepared by flux-assisted melting using fluoride salts. Particle size was kept below 1 μm in case of TiB_2 and TiC and around 10 μm in case of $TiAl_3$. The purity of the metal was 99.85%. All the materials were produced in a graphite crucible at 800°C (Al-TiB_2 and Al-$TiAl_3$) or 1200°C (Al-TiC) [6].

The composites were foamed as-cast or after further dilution with liquid metal. Foams were made in Al_2O_3 crucibles by admixing 1.6 wt.% of untreated TiH_2 blowing agent into 30 to 60 g of melted precursor at 700°C, while vigorously stirring at 900 rpm. After mixing, the foam was isothermally held for up to 50 s and then cooled with pressurized air. Particle type and content of the various foaming experiments are shown in Table 1.

Foam structure was recorded both ex-situ and in-situ by X-ray radioscopy using a microfocus X-ray source and a panel detector as described in Ref. [7]. For in-situ experiments the foam evolution was interrupted in early stages and a piece of the sample was remelted at 700°C in our X-ray radioscope on a ceramic heater plate.

For microstructural characterisation samples were cut and polished with SiC paper followed by polishing with a diamond suspension.

TABLE I. Particle contents of the foaming experiments.

#	particle type	particle content, vol. %
1	none	0
2	$TiAl_3$	11.5
3	TiB_2	6
4	TiB_2	2
5	TiC	4

RESULTS AND DISCUSSION

Blowing pure Al with TiH_2 did not lead to foam although some bubble residues remained on the top of the sample. The Al-$TiAl_3$ composite could also not be successfully foamed and the particles did sediment in the melt instead of attaching to the bubbles. In contrast, the Al-TiC composite melt could be used as a useful precursor for foam as is observed in Fig. 1(a,b). Al-TiB_2 composites led to a foam showing less drainage compared to the one stabilized with TiC, see Fig. 2(a). Diluting the TiB_2-containing composite with pure aluminium reduced the amount of the foam as becomes evident from Fig. 2(b). Significant drainage was observed after aluminium addition, see Fig. 2(b). Diluting the TiC-containing composite with pure aluminium produced the similar detrimental effect as for Al-TiB_2 composites.
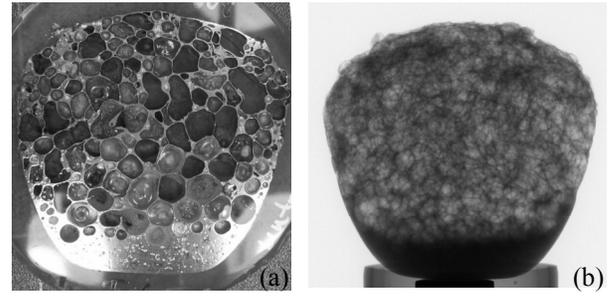
Figure 1. (a) Cross section and, (b) X-ray image of TiC stabilized foam (#5). Bottom part of the foam is 30 mm wide.
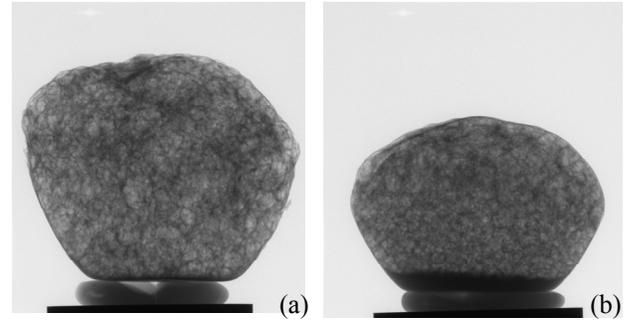
Figure 2. X-ray images of Al-TiB_2 composite foam after 200 s of holding (a) without Al dilution (6 vol.% of TiB_2 particles = #3) and (b) with Al dilution to 2 vol.% TiB_2 (#4), both foamed with untreated TiH_2. Bottom part of the foam is 30 mm wide.

Scanning electron microscopy of foam containing TiB_2 particles showed aluminium dendrites and interdendritic regions filled with TiB_2 particles as shown in Fig. 3(a) and (b). In small pores at the beginning of pore formation, the surface is partly covered but as the pores becomes bigger, the TiB_2 particles cover the whole surface of the bubble.

EDX-based Ti mapping of the sample confirmed the presence of TiB_2 particles both on the surface of the bubble and in the interdendritic regions. TiC stabilised foams have typical cell wall thicknesses around 70 μm, see Fig.4(a). Only few TiC particles can be found inside the cell walls and the particles are not interconnected, see Fig. 4(b). The surface of the cell wall is densely covered with them.

The above results indicate that the use of TiB_2 and TiC particles improves foamability of aluminium. It is also remarkable that all the abovementioned particles lead to grain refinement in Al and Al alloys as is evident from the previous studies of the authors [6]. Thus there appears to be
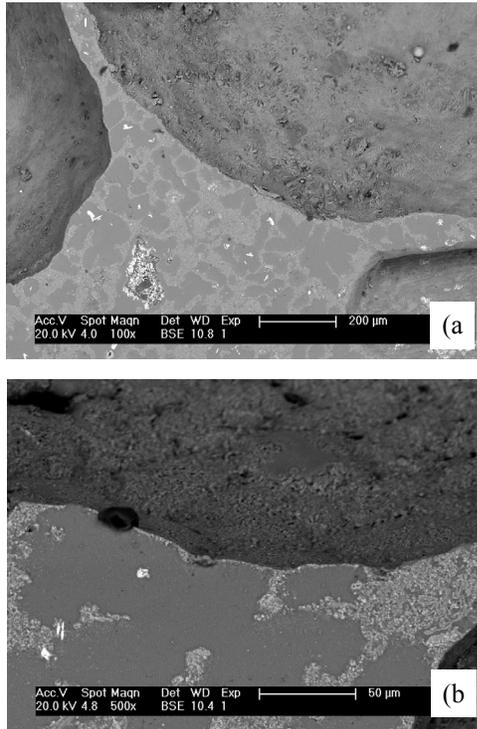
Figure 3. SEM images of Al-TiB$_2$ foam showing (a) cell walls and a Plateau border with TiB$_2$ particles in inter-dendritic regions, (b) TiB$_2$ layer segregated on cell surface.
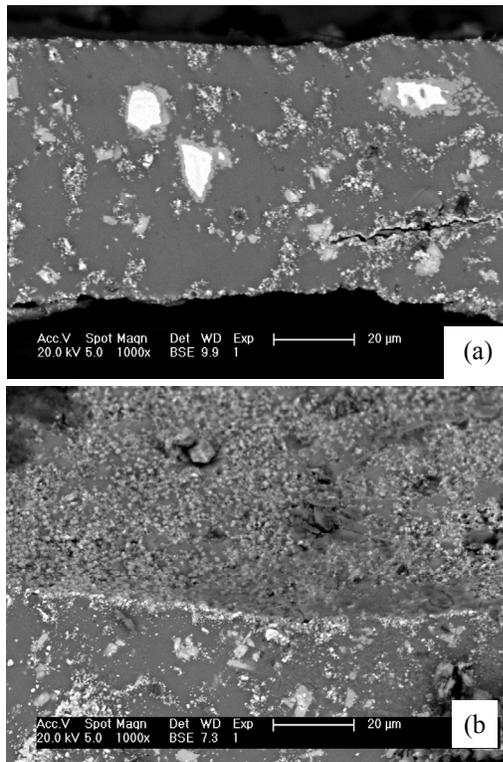
Figure 4. SEM images of Al-TiC foam showing (a) TiC particles at the cell wall, (b) enlarged view of the cell wall decorated with TiC particles.

a 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 for crystallisation depends on a number of parameters such as its crystal structure, number of available crystallographic planes that can act as substrates for nucleation, facetted 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.

Data on the wetability of TiAl$_3$ by Al is not available, while Kaptay [8] 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 wetability of the two particles from the above report. TiAl$_3$ has a tetragonal structure and is known not to be 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 particle types and appear to be unable to segregate to the bubble surface and hence cannot act as a good stabiliser of foam. Though TiB$_2$ has a contact angle of $0°$ in vacuum at 1100°C, the finer particles 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 TiB$_2$. Accordingly, it has a stronger surface activity and thus segregates to the bubble resulting in its stabilisation. Due to the smaller contact angle significant amounts of TiB$_2$ particles remain inside the cell wall, but the surface of the bubbles is still completely covered. Thus, TiB$_2$ should have two effects, namely as surface active particle increasing surface elasticity and as a particle located in the bulk inbetween the two gas/metal interfaces slowing down drainage.

Attempts to foam pure Al were not successful, which further strengthens the idea that particles are necessary to stabilise liquid metal foams [1]. 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. TiH$_2$ particles have been observed at some cell walls and 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. A similar result was reported for AlMg20 alloys with 10 wt% TiH$_2$ addition [9]. 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 [10] although larger particles (70 μm) did not lead to stable foams in the Formgrip process [11]. 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 significantly smaller than the cell wall thickness the effect of the surface segregation can be observed more clearly.

The study on foam evolution of TiB$_2$ composite indicated that the foam has high stability (Fig.5).
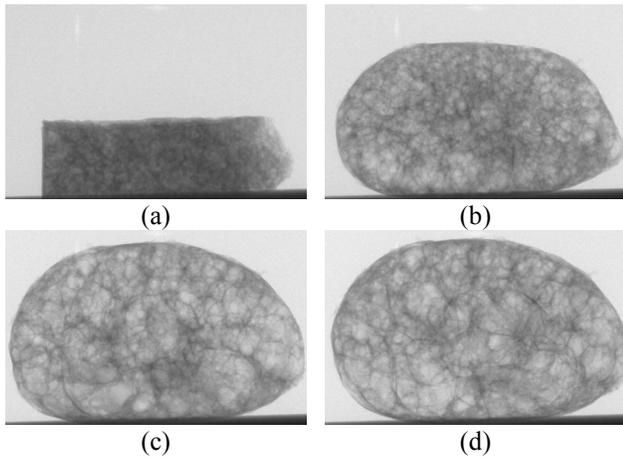
Figure 5. TiB$_2$ stabilized foam evolution: (a) precursor in solid state, (b) foamed and melted precursor at 700°C after 100 s, (c) after 200 s and (d) after 600 s holding.

The foam structure remained nearly intact even after 600 s of holding which is significantly more compared to Alporas-type foams where foam collapse starts after 100 to 200 s of holding [12, 13]. The stabilising bi-films do not show surface segregation in Alporas foams as we have revealed in our previous study [14]. The larger stabilization ability of our grain refiner type particles could originate from the surface segregation behaviour of the TiB$_2$ and TiC particles which are acting through a different stabilizing mechanism as the particle bridging mechanism in powder metallurgical (PM) and Alporas foams.

SUMMARY

Aluminium foams were successfully produced using precursors made by flux-assisted melting using fluorides. TiB$_2$ and TiC particles proved to be good foam stabilisers, whereas TiAl$_3$ did not lead to any foam although the particles remained in the precursor. Ex-situ characterisation of the foams by SEM showed that both TiB$_2$ and TiC particles segregate to the surface of the cell walls leading to an almost dense coverage. It has been demonstrated that metal foams can be stabilised by sub-micrometre particles and that their stability is influenced by the addition of alloying elements. 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. The stability of the new additive is significantly higher than that of Alporas-type precursors which originates from a different stabilizing mechanism of the particles compared to PM and Alporas foams.

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