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Journal of Alloys and Compounds

# AlB<sub>3</sub> master alloy to grain refine AlSi10Mg and AlSi12Cu aluminium foundry alloys

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#### ARTICLE INFO

## ABSTRACT

Article history: Received 2 September 2011 Received in revised form 1 October 2011 Accepted 3 October 2011 Available online 17 October 2011

*Keywords:* Aluminium alloys Grain refinement The potential of AlB3 master alloy in the grain refinement of AlSi10Mg and AlSi12Cu foundry alloys was investigated and compared with that of the AlTi5B1 master alloy, the standard grain refiner for most aluminium foundries. The latter refines the grain structures of both alloys. However, this performance is not nearly as good as that obtained in wrought aluminium alloys with the same grain refiner. The Ti-free AlSi10Mg and AlSi12Cu alloys, on the other hand, exhibit very small grains for the entire range of holding times when inoculated with AlB3. This implies a remarkable grain refining efficiency, typical of grain refined wrought aluminium alloys, as well as a strong resistance to fading of the grain refinement effect. Lack of Ti in the melt allows the entire B to form AlB<sub>2</sub> particles, the perfect substrates, shortly before  $\alpha$ -Al starts to crystallize. Aluminium castings can enjoy grains as small as those of the wrought alloys, well below 200  $\mu$ m, with an addition of 0.02 wt% B provided that their Ti content is controlled.

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## 1. Introduction

Grain refinement is a critical operation in aluminium foundries that impacts not only the quality of the cast part but also the efficiency of the casting process [1–5]. It is thus a standard practice in aluminium foundries world-wide to add master alloys to molten aluminium in order to achieve fine, equiaxed grains after solidification.

Titanium nucleates aluminium thanks to a peritectic reaction in the Al-rich corner of the Al-Ti binary system. However, this peritectic reaction dictates a minimum Ti concentration of 0.15 wt%. The grain refinement efficiency has been shown in late 1940s to increase markedly when B is also added to molten aluminium, allowing the same level of refinement at much lower Ti additions [6]. Al-Ti-B master alloys have thus been the standard grain refiners for aluminium alloys eversince [7-11]. These grain refiners offer a remarkable performance in the continuous and semi-continuous casting of wrought alloys, yet fail to meet the expectations in the case of aluminium foundry alloys [12,13]. The latter contain substantial levels of Si to improve castability. Si, the major ingredient of the foundry alloys, reacts with Ti to form Ti-Si binary phases at Si > 3 wt%, at the expense of Al<sub>3</sub>Ti and TiB<sub>2</sub> particles, thereby imparing the grain refinement efficiency [14-17]. In contrast to the wrought alloys which are grain refined adequately at Ti addition rates of 0.005-0.01 wt%, foundry alloys require at least 10 times more of the same grain refiner. While excessive additions compensate for the relatively poor efficiency of the Al–Ti-B grain refiners to a certain extent, it is neither attractive nor economic to use so much grain refiner in shape casting.

Aluminium foundries need more potent grain refiners for sound castings of better quality at competitive cost since the automotive manufacturers are increasingly more demanding on quality issue. The grain refinement of aluminium foundry alloys can be accomplished only with grain refiners that are potent in spite of high Si levels. While Al–B master alloys were shown to be more effective with Al–Si alloys [10,13,14,18–20], the industrial practice today relies almost entirely on the AlTi5B1 grain refiner. The search for alternative grain refiners and more effective grain refinement practices has intensified in recent years [21–24]. The present work was undertaken to investigate the potential of AlB3 master alloys in the grain refinement of AlSi10Mg and AlSi12Cu foundry alloys.

#### 2. Experimental

The chemical analysis of the commercial AlSi10Mg and AlSi12Cu ingots used in the present work are listed in Table 1. Low pressure die casting process is employed to manufacture cylinder heads and clutch housings from these two alloys. The grain refiner additions in a typical industrial operation are made once the furnace operations are over, just before the melt is transferred to the low pressure die casting unit. They are grain refined with the addition of 2.2 and 4 kg of AlTi5B1 into 600 kg of molten AlSi10Mg and AlSi12Cu alloys, respectively. The relatively higher addition rate for the latter is linked with the fact that it is relatively more difficult to grain refine the AlSi12Cu alloy owing to its higher Si content.

AlSi10Mg and AlSi12Cu alloys were grain refined in the laboratory first in exactly the same manner with the aluminium foundries. The grain refiner master alloy was a commercial AlTi5B1 grade used by most aluminium foundries in Turkey. Its microstructure is typical of AlTi5B1 alloys with predominantly blocky Al<sub>3</sub>Ti and

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Table 1

Chemical analysis of the alloys used in the grain refinement experiments (wt%).

Alloy	Si	Fe	Cu	Mn	Mg	Zn	Ti	В
AlSi10Mg	10.62	0.043	< 0.001	< 0.010	0.135	0.016	0.1140	0.0005
AlSi12Cu	11.89	0.740	1.898	0.384	0.217	0.971	0.0450	0.0006
AlSi10Mg <sup>a</sup>	10.73	0.048	< 0.001	< 0.010	0.131	0.018	0.0046	0.0003
AlSi12Cu <sup>a</sup>	11.94	0.782	1.902	0.376	0.216	0.964	0.0048	0.0002

<sup>a</sup> Experimental alloys prepared in the laboratory.



Fig. 1. Microstructures of (a) the AlTi5B1 and (b) AlB3 grain refiners used in the present work.

a fine dispersion of TiB<sub>2</sub> particles (Fig. 1a). The Ti addition rates were 0.018 and 0.033 wt% for AlSi10Mg and AlSi12Cu alloys, raising the Ti contents of the molten alloys to approximately 0.075 and 0.125 wt%, respectively. The temperature of the melt at the time of grain refiner addition, 750 °C, was adopted from the industrial practice. The melt was stirred with a graphite rod for 20s right after grain refiner addition. Samples were taken from the melt 2, 5, 10, 15, 30 and 60 min after the addition and were solidified in small copper molds with a diameter of 25 mm and a height of 50 mm.

The grain refined samples were sectioned 20 mm from the bottom surface. This is exactly where the solidification rate was estimated from secondary dendrite arm spacing measurements to be similar to that encountered in the flame deck of the cylinder heads facilitating a fair comparison with the industrial practice. Standard metallographic procedures were employed to prepare these sections for grain size measurements. They were etched with Poulton's reagent and were then examined under a light microscope. The same series of samples were also anodised in Barker's solution, 5 ml HBF4 (48%) in 200 ml water, and then examined with an optical microscope method.

The next part of the work relied on the addition of AlB3 master alloy for grain refinement. However, the commercial alloy ingots are supplied with as much as 400–1000 ppm Ti (Table 1). Al-B addition into the commercial alloys would be practically not much different from adding a ternary Al–Ti-B grain refiner since the B supplied is readily and entirely transformed to TiB<sub>2</sub> particles [20]. Hence, the Ti-free versions of the two foundry alloys of the present work were produced in the laboratory with identical compositions but with less than 0.005 wt% Ti (Table 1). Aluminium ingot with a purity of 99.85 wt% Al, commercial purity silicon and magnesium were used to produce the Ti-free AlSi10Mg while additionally Al50Cu50 master alloy was used to prepare the Ti-free AlSi12Cu alloy ingot. Pre-calculated masses of the ingredients were melted in an electric resistance furnace and held at 800 °C for 1 h to allow homogenization and were finally cast into copper-based permanent molds for rapid solidification in order to avoid segregation.

The AlSi10Mg and AlSi12Cu alloy ingots thus obtained, each weigthing 1000 g, were melted in a resistance furnace and the temperature of the melts thus obtained were brought to 750 °C. Grain refinement tests were performed with the AlB3 master alloy that contains only AlB<sub>2</sub> particles in contrast to the AlTi511 alloy [14] (Fig. 1b). The AlB3 grain refiner was then added so as to bring the B concentration of 1 kg AlSi10Mg and AlSi12Cu melts to 0.02 wt% B. The grain refinement experiments and the metallographic procedures to analyze the grain structures were conducted in exactly the same manner employed in the first part of the study.

### 3. Results and discussion

The grain structure of the unrefined AlSi10Mg alloy is coarse with an average grain size of approximately 1450  $\mu$ m (Figs. 2 and 3). The commercial practice has introduced a nearly 3-fold refinement of the grain structure with an average grain size of 415 µm 2 min after inoculation. However, the AlTi5B1 grain refiner provides much smaller grains, almost always smaller than 200 µm in wrought aluminium alloys at the same addition rate [20]. A second shortcoming of the AlTi5B1 grain refiner with the AlSi10Mg alloy is the relatively stronger fade effect. The cast grains become increasingly coarse with time after grain refiner addition contrasting wrought aluminium alloys which enjoy very fine grains even 60 min after refiner addition. The more pronounced fading of the grain refinement is linked with the high Si content of the foundry alloys which promote the settlement of the TiB<sub>2</sub> particles due to a much higher fluidity. Considering that the melt is sampled from the top of the crucible, in a manner similar to that employed in the low pressure die casting of critical structural castings, the melt sample is inevitably depleted off its borides when the contact time is too long.

The cast grains of the unrefined AlSi12Cu alloy are even bigger (approximately 1750  $\mu$ m) and predominantly columnar near the edges (Figs. 2 and 3). It is well established that the grain size of aluminium foundry alloys increases with increasing Si above 5 wt% [19]. The grain structure is refined upon the addition of AlTi5B1 master alloy at an addition rate of 0.033 wt% Ti. With an average grain size of 650  $\mu$ m 2 min after grain refiner addition, the performance of the AlTi5B1 alloy is nearly identical in AlSi10Mg and AlSi12Cu alloys. However, this performance is clearly inferior with respect to that achieved in wrought aluminium alloys, where grains smaller than 200  $\mu$ m are typical. The difference in the performance becomes even more evident when the final Ti levels of the two alloys, 0.02 wt% vs 0.12 wt%, are considered.

When inoculated with the AlB3 master alloy, the grains of the Ti-free AlSi10Mg alloy are very fine, uniform and nearly globular for the entire range of holding times, implying a remarkable grain refining efficiency (Figs. 2 and 3). The grain size is comparable to those obtained in grain refined wrought aluminium alloys. A further advantage of adding 200 ppm B into a Ti-free melt appears to be



Fig. 2. Grain structures of (a) AlSi10Mg and (b) AlSi12Cu alloys before and after the addition of AlTi5B1 and AlB3 grain refiners. Grain structures of (c) AlSi10Mg and (d) AlSi12Cu alloys before and 2 min after the addition of AlTi5B1 and AlB<sub>3</sub> grain refiners, as revealed by the Barker's etch.

the strong resistance to fading of the grain refinement effect. The average grain size 60 min after grain refiner addition is  $125 \pm 16 \,\mu$ m (Fig. 3). AlB3 produces very fine grains also in the Ti-free AlSi12Cu alloy (Figs. 2 and 3). The refined grain structure (average grain size is  $128 \pm 21 \,\mu$ m 2 min after addition) survives for up to 60 min with no evidence of fading (Fig. 3). It is fair to conclude from the foregoing that AlB3 is an outstanding grain refiner for the Ti-free AlSi10Mg and AlSi12Cu alloys.

Foundry alloys are almost invariably alloyed with Ti with the intention to control the cast grain size. However, it has been shown recently that the favourable impact of Ti on grain refinement is severely impaired at Si > 5 wt% [19]. Solute Ti, which is known to be the most effective growth restrictor for aluminium [25], is rendered ineffective as it forms Ti–Si compounds and precipitates out of the melt. The majority of the foundry alloys, on the other hand, contain more Si and have to bear the consequences. Further addition into the melt of the soluble TiAl<sub>3</sub> and the insoluble TiB<sub>2</sub> particles through the addition of the AlTi5B1 grain refiners provide only a modest improvement. TiB<sub>2</sub> particles are also poisoned by Si that coats their surfaces with Ti–Si compounds.

The inadequate grain refinement of foundry alloys can be circumvented by the use of Al-B binary, instead of Al–Ti-B ternary, grain refiners when casting foundry alloys. AlB3 supplies only AlB<sub>2</sub> particles, which serve as very potent substrates for  $\alpha$ -Al nucleation, provided that the melt does not contain Ti. This is evidenced by the remarkable performance of the AlB3 grain refiner with the Ti-free AlSi10Mg and AlSi12Cu alloys in the present work. AlB<sub>2</sub> particles dissolve readily in Al–Si melts and form again when the melt starts to cool for solidification. The grains of Ti-free AlSi10Mg and AlSi12Cu alloys are refined through the heterogeneous nucleation of  $\alpha$ (Al) on AlB<sub>2</sub> particles. Analysis of the Al-rich corner of the calculated Al–Si-B liquidus surface suggests that the primary AlB<sub>2</sub> is formed at a Si concentration of approximately 4 wt% [20]. It is thus



**Fig. 3.** Grain size measurements of the commercial and Ti-free (a) AlSi10Mg and (b) AlSi12Cu alloys before and after AlTi5B1 and AlB3 grain refiner additions.

inferred that AIB master alloys are capable of grain refining the majority of aluminium foundry alloys. There is hardly any fading risk since the AlB<sub>2</sub> particles form just before the nucleation of  $\alpha$ -Al crystals [19]. This is clearly a further advantage of the Al-B based grain refiners when Al-Si foundry alloys are to be recycled. The B content of the latter is not critical as long as the dosing is tuned to provide sufficient B in the melt [18].

It is fair to conclude from the foregoing that the foundry alloy ingots must be produced without Ti to facilitate an outstanding grain refinement with the addition of only 200 ppm B. This is indeed very attractive not only from an economic standpoint but also for those applications where the conductivity of aluminium alloys is essential.

#### 4. Conclusions

The performance of AlTi5B1, identified to be the best grain refiner for wrought aluminium alloys, falls short of expectations with the AlSi10Mg and AlSi12Cu foundry alloys. The grains of the Ti-free AlSi10Mg and AlSi12Cu alloys, on the other hand, are very small for the entire range of holding times when inoculated with AlB3, implying a remarkable grain refining efficiency as well as a strong resistance to fading of the grain refinement effect. Lack of Ti in the melt allows the entire B to form AlB<sub>2</sub> particles, the perfect substrates, shortly before  $\alpha$ -Al starts to crystallize. Aluminium castings can enjoy grains as small as those of the wrought alloys, well below 200  $\mu$ m, with an addition of 0.02 wt% B provided that their Ti content is controlled.

#### Acknowledgements

It is a pleasure to thank Mr. O. Cakir for performing grain refining performance tests and Mr. F. Alageyik for metallographic work. This work was supported by TUBITAK.

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