INFLUENCE OF AlNb3.5B0.4 GRAIN REFINEMENT ON THE PRECIPITATION OF Fe-RICH INTERMETALLICS IN A SECONDARY AlSi7Mg ALLOY

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Abstract

Aluminum-silicon alloys are important materials in foundry to produce light components to be used in the automotive industry for weight saving, reduction of carbon emission from vehicles and air pollution. The mechanical properties of these alloys are strictly related to the final microstructure that can be improved by grain refinement. However, the addition of specific grain refiners can promote the formation of Fe-rich compounds with platelet morphology, which can significantly affect the ductility of the alloy. In the present research, the effect of AlNb3.5B0.4 grain refiner on the formation of Fe-rich intermetallics in a secondary AlSi7Mg alloy was investigated. Metallographic and image analysis techniques were used to quantitatively investigate the microstructural variations occurring with the addition of grain-refining agent at different cooling rates. The results show that the α-Fe compounds are the dominant Fe-rich phase in the secondary AlSi7Mg alloy. On the other side, the addition of AlNb3.5B0.4 grain refiner promotes the precipitation of β-Fe platelets at the expense of Chinese script α-Fe particles. This mechanism is even more evident at higher cooling rates. The AlNb3.5B0.4 grain refinement significantly affects the number density of β-Fe compounds but it does not influence their dimensions. The size of β-Fe particles appears to be sensitive to the change of the cooling rate; higher cooling rate refines the microstructural scale as well as the Fe-rich platelets. The addition of AlNb3.5B0.4 produces a fine and uniform grain structure throughout the alloy and this effect is more pronounced in the slowly solidified material. Increasing the cooling rate, lower amounts of grain refiner are needed to produce a uniform grain size throughout the casting.

Keywords: Aluminum alloy, Fe-rich intermetallic, niobium, boron, microstructure

1.   INTRODUCTION

After solidification of Al-Si alloys, coarse and columnar grain structure is usually observed unless the melt solidifies with a high cooling rate. Coarse grains may result in many types of defects, reduction of yield strength and ductility. Fine and equiaxed grain structure can be produced by the addition of a number of elements, such as Ti, B, Zr, Nb into the melt. The addition of the grain refiner increases the number of heterogeneous nucleation sites in the molten metal; these are usually aluminides or borides formed by peritectic reaction, and the nucleation density is thus increased during the solidification resulting in grain refined microstructure. It is reported that fine and equiaxed grain structure guarantees better surface finish, advanced mechanical properties, finer microporosity, better dispersion of secondary phases, improved feeding and fluidity [1].

In the current foundry practice, chemical grain refinement is commonly accomplished by the introduction of master alloys into the molten bath. Grain refiners usually contain Ti and/or B with various Ti/B weight ratios, such as Al-5Ti, Al-4B, Al-5Ti-1B, Al-3Ti-3B, Al-1Ti-3B. Although there is still a great discussion about the efficiency of those master alloys, the general conclusion is that the effect of grain refinement is more remarkable by using Al-B or Al-Ti-B with a Ti/B ratio lower than 1:1 because of the interaction between Ti and

Si reducing the effective quantity of Al_3Ti and TiB_2 nucleants [2]. A new generation of master alloys, such as Al-Zr, Al-Ti-C, Al-Nb-B, are used in grain refinement where Al_3Zr, TiC, Al_3Nb and NbB_2 phases are the main nucleants of α-Al phase. The Al_3Zr phase has been found to be less effective than the Al_3Ti phase on the grain refinement [3]. Although Al-Ti-C master alloy shows lower agglomeration tendency with respect to Al-Ti-B system, the TiC phase might be faded because it is thermodynamically unstable and can be poisoned by Si [4]. The NbB_2 phase is much more stable than TiB_2 particles, showing therefore greater efficiency on grain refinement [5]. In recent years, lanthanides, such as La, Ce, Gd, have shown the potency of grain refinement of Al-Si alloys too. On the other hand, they have a matter of cost in use and tend to fade [6].

Grain refiner can interact with alloying elements and impurities present in the initial alloy. Several investigations conclude that Ti interacts with minor additions and impurities, such as Sr, Zr, Cu, and Fe as well as with Si, resulting in a coarser α-Al structure [7–10]. Among all impurities, iron is one of the most harmful in Al-Si foundry alloys, especially in the form of β-Al_5FeSi platelets, which increase the alloy embrittlement. The sharp edges of β phase generate high-stress concentrations, resulting in the formation of cracks and the decrease of mechanical properties [11].

Understanding the effect of grain refiner addition on the formation of Fe-rich compounds is of great importance to improve the final casting quality. Previous works focused on the influence of AlTi5B, AlTi10, Al5B grain refiners on the Fe-rich phases [12,13]. On the other side, the studies on the effect of Nb-B inoculant on the precipitation of iron-rich particles in Al-Si alloys are limited.

This study aims to analyse the influence of different levels of Al-3.5Nb-0.4B grain refiner on the precipitation of Fe-rich intermetallics in secondary Al-7Si-0.3Mg alloy.

2.   EXPERIMENTAL PROCEDURE

2.1.   Casting procedure

A secondary AlSi7Mg cast alloy (EN AB-42000) in the form of commercial ingots was used as the base alloy and its chemical composition is shown in **Table 1**. An AlNb3.5B0.4 master alloy in rod shape was used as a grain refiner and added at two different levels (0.3 and 1.4 wt%) in order to obtain nominal Nb contents of 100 and 500 wt. ppm Nb and nominal B levels of 13 and 55 wt. ppm B. The experimental chemical composition of the grain refined alloy is listed in **Table 1**. About 3.5 kg charge of AlSi7Mg alloy was melted at 750 °C in a SiC crucible in a resistance-heated furnace. The molten bath was gently skimmed and stirred before each addition, and it was held at 750 °C for 30 min to ensure the complete dissolution of the grain refiner addition. The melt was poured at 750 °C into two different boron nitride-coated steel moulds: a cylindrical-shaped die with an inner diameter of 20 mm and height of 100 mm, and a truncated conical cup with a lower diameter of 45 mm, an upper diameter of 70 mm and height of 60 mm. Both dies were preheated at 550 °C. The cylindrical-shaped mould provides a higher cooling rate of 1.3 °C/s, while the truncated conical cup provides a lower cooling rate of 0.1 °C/s. No degassing treatment was performed before casting operations.

Table 1 Chemical composition (wt%) of the investigated alloys

	Al	Si	Fe	Cu	Mn	Mg	Zn	Ti	Nb	B
AlSi7Mg (base alloy)	Bal.	7.36	0.43	0.055	0.29	0.35	0.05	0.021	0	0.0001
AlSi7Mg + 0.3 wt% AlNb3.5B0.4	Bal.	7.34	0.43	0.055	0.29	0.35	0.05	0.021	0.0106	0.0013
AlSi7Mg + 1.4 wt% AlNb3.5B0.4	Bal.	7.25	0.44	0.053	0.30	0.31	0.05	0.020	0.0504	0.0055

2.2. Metallographic characterization

The cylindrical sample was transversely cut at 25 mm from the bottom surface, while the sample with a cooling rate of 0.1 °C/s was sectioned longitudinally in half to extract a surface for the microstructural investigation. Both samples were then mounted, ground, and polished according to standard metallographic techniques. Optical (OM) and scanning electron microscopes (SEM) were used to measure the secondary dendrite arm spacing λ_2 and to characterize the distribution of the size and morphology of the Fe-rich phases in the microstructure. To obtain a statistical average of the distribution, the series of different micrographs of each specimen were taken covering a region of interest of 8 mm^2; each measurement included more than 400 particles.

To improve the contrast between the Fe-rich phases and other phases in the microstructure, the polished samples were chemically etched in an aqueous sulphuric acid solution at 70 °C (20 vol% H_2SO_4 and 80 vol% H_2O). For the measurement of the grain size, the polished specimens were firstly etched in a $CuCl_2$ solution (30 vol% $CuCl_2$ and 70 vol% H_2O) and then immersed in nitric acid solution (86 vol% HNO_3 and 14 vol% HF). The grain size was measured using the intercept method, according to ASTM standard E112-12.

3. RESULTS AND DISCUSSION

Figure 1 shows the typical microstructure of AlSi7Mg alloy after the addition of AlNb3.5B0.4 grain refiner. In general, the microstructure of both AlSi7Mg alloy and grain refined AlSi7Mg alloys consists of a primary phase, α-Al solid solution in the form of dendrites, and a eutectic mixture of aluminum and silicon. Intermetallics compounds, such as Fe- and Mg-rich intermetallics, are also observed. The Fe-rich compounds show needle-like or Chinese script morphology. After 1.4 wt% AlNb3.5B0.4 addition, polygonal Nb-rich particles are observed in the microstructure, especially at a lower cooling rate (see **Figure 1**).
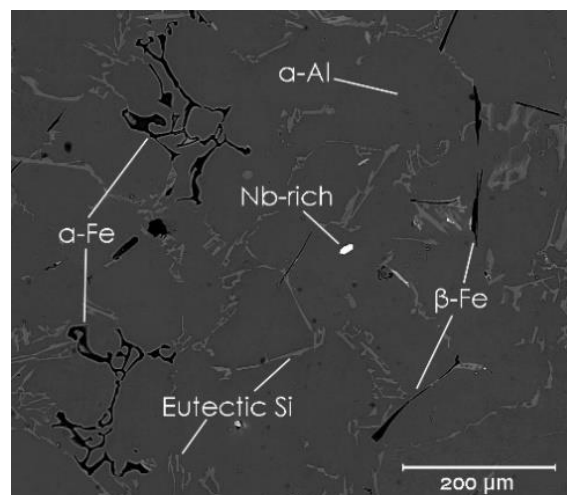

Figure 1 Backscattered SEM micrograph of AlSi7Mg alloy after AlNb3.5B0.4 grain refinement

For both casting geometries, the scale of the microstructure was evaluated by means of λ_2 measurements. As expected, the casting geometry of the samples significantly affected the cooling rate, which varied in the range of 36 and 72 μm. The alloy solidified at a higher cooling rate, i.e. 1.3 °C/s, showed a microstructure scale with λ_2 values of 36±3 μm. On the other side, the alloy solidified at a lower cooling rate, i.e. 0.1 °C/s, showed λ_2 value of 72±5 μm.

Figure 2 shows the microstructures of the AlSi7Mg and the grain refined AlSi7Mg alloys at different cooling conditions. In the AlSi7Mg alloy, the α-Fe phase is the dominant phase among the Fe-rich compounds independently of the cooling rate. The addition of AlNb3.5B0.4 grain refiner promotes the formation of needle-like Fe-rich compounds whose size is strongly affected by the cooling rate.
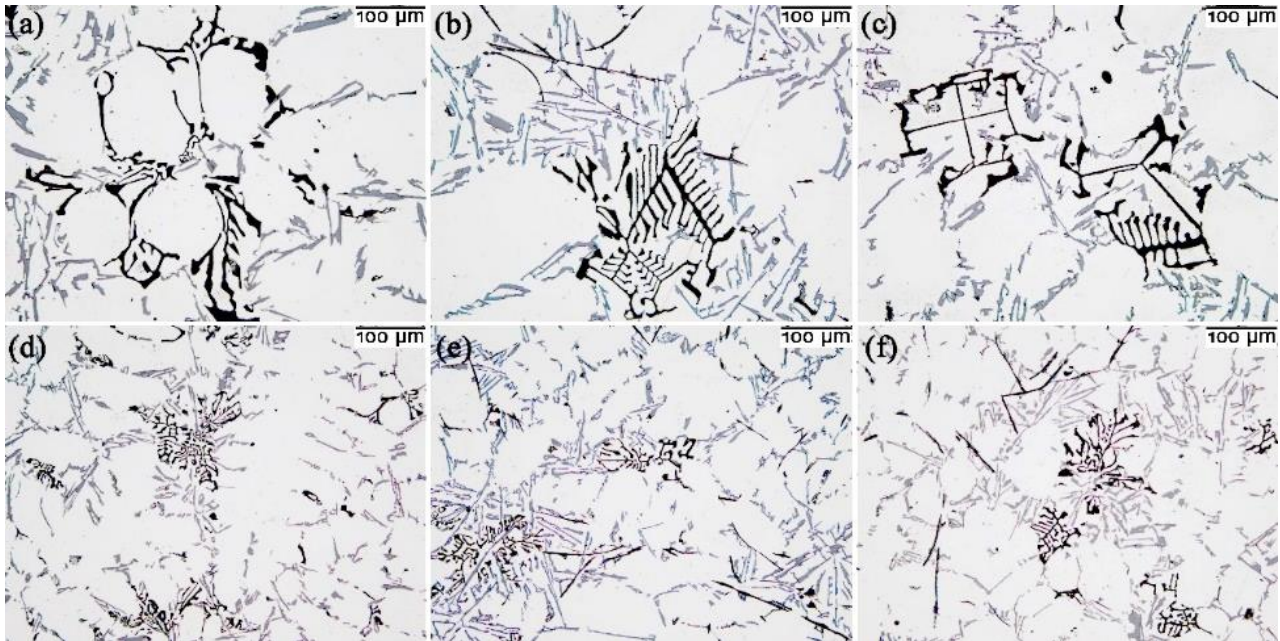
Figure 2 Typical etched microstructures of **(a, d)** the AlSi7Mg alloy and the grain refined AlSi7Mg alloys after **(b, e)** 0.3 and **(c, f)** 1.4 wt.% AlNb3.5B0.4 additions. The micrographs correspond to specimens solidified at **(a-c)** 1.3 and **(d-f)** 0.1 °C/s cooling rate

Figure 3 presents the statistical analysis of the size and number density of β-Fe particles in the AlSi7Mg alloy at various AlNb3.5B0.4 levels and solidified at different cooling rates. Upon increasing the cooling rate in the AlSi7Mg alloy, the length of β-Fe particles with the maximum frequency shifts to lower values and the absolute value of the maximum frequency increases. The average length moves from about 35 to 17 μm at lower and higher cooling rates, respectively. Similar behaviour can be observed for the number density of the β-Fe phase (**Figure 3c**). These results are in agreement with the findings from Rakhmonov et al. [12]. When the cooling rate increases, the time for intermetallic particles to grow and coarsen decreases because the nucleation temperature of the β-Fe phase is displaced toward lower temperatures, resulting in smaller and shorter Fe-rich compounds.

This phenomenon is even more evident after the AlNb3.5B0.4 grain refinement. The addition of Nb-B inoculant emphasizes the precipitation of β-Fe particles but does not significantly affect the average size of the β-Fe needles (**Figures 3a and b**).
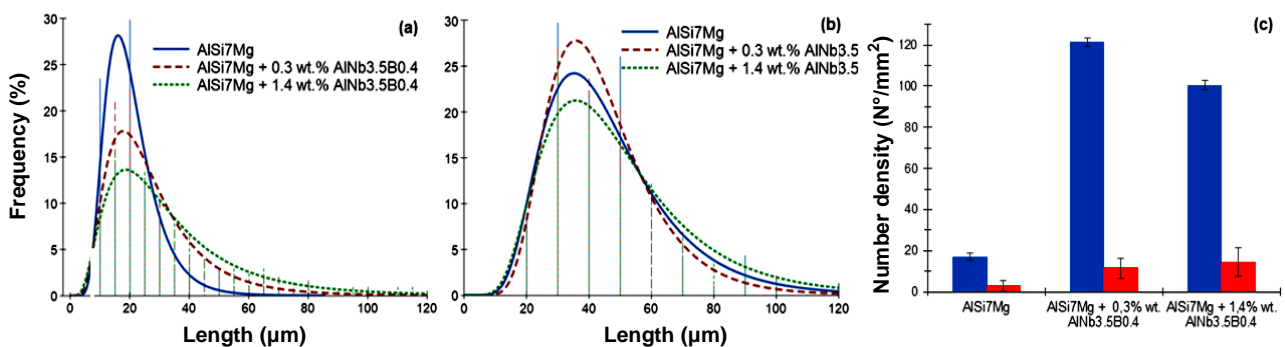

Figure 3 Distributions of the length of β-Fe particles in the AlSi7Mg alloy and grain refined AlSi7Mg alloys solidified at different cooling rates: **(a)** lower and **(b)** higher (lognormal fitting curves are drawn).**(c)** Number density of β-Fe particles as function of the AlNb3.5B0.4 level and cooling rate

Figure 4 shows the area fraction of both α-Fe and β-Fe phases as a function of the AlNb3.5B0.4 level and the cooling rate. In the AlSi7Mg alloy, the α-Fe phase appears as the main Fe-rich phase regardless of the cooling rate. In fact, the area fraction of the α-Fe phase is higher than 1.28% and the area fraction of the β-Fe phase is lower than 0.065% at both cooling rates. This result can be explained considering the cooling rate and the chemical composition of the AlSi7Mg alloy. The Mn/Fe ratio is 0.68, higher than 0.5, which is the critical value to suppress the formation of the β-Fe compounds [14]. This ratio is almost the same also in the refined alloys. It can be therefore assumed that the addition of AlNb3.5B0.4 grain refiner promotes the precipitation of β-Fe phase.

Either in the AlSi7Mg alloy or in the grain refined AlSi7Mg alloys, the Fe-rich compounds, both α- and β-Fe phases, are well distributed throughout the microstructure, comprising about 1.5±0.3% of the total investigated area. As previously mentioned, the formation of different types of iron intermetallics depends on the cooling rate and the chemical composition of the alloy. At 1.3 °C/s, the area fraction of the α-Fe phase in the AlSi7Mg alloy corresponds to 1.297 % and this value decreases to 0.834 and 1.025 % in the alloys modified with 0.3 wt% and 1.4 wt% AlNb3.5B0.4, respectively. At 0.1 °C/s, the area fraction occupied by β-Fe phase increases from 0.050% in the AlSi7Mg alloy to 0.189% and 0.267% after the grain refinement with 0.3 wt% and 1.4 wt% AlNb3.5B0.4, respectively. It must be noted that the addition of AlNb3.5B0.4 grain refiner increases the precipitation of β-Fe, especially at high cooling rates. Rakhmonov et al. [13] suggested that the limited precipitation of β-Fe in the AlSi7Mg alloy is related to higher undercooling required for the nucleation of this phase. In contrast, the presence of heterogeneous sites, such as TiB_2 particles in the refined alloy, facilitates the β-Fe precipitation at low undercooling. Moreover, a greater undercooling reduces the Fe content involved in the crystallization of α-Fe phase and increases the level of Fe available for β-Fe formation. In this study, the addition of Nb-B inoculant promotes the formation of particles which lead to the heterogenous nucleation of the β-Fe phase. Since Ti content in both base and refined alloys is low, Ti_2B particles, which may be formed in a small amount, cannot significantly affect the precipitation of β-Fe.
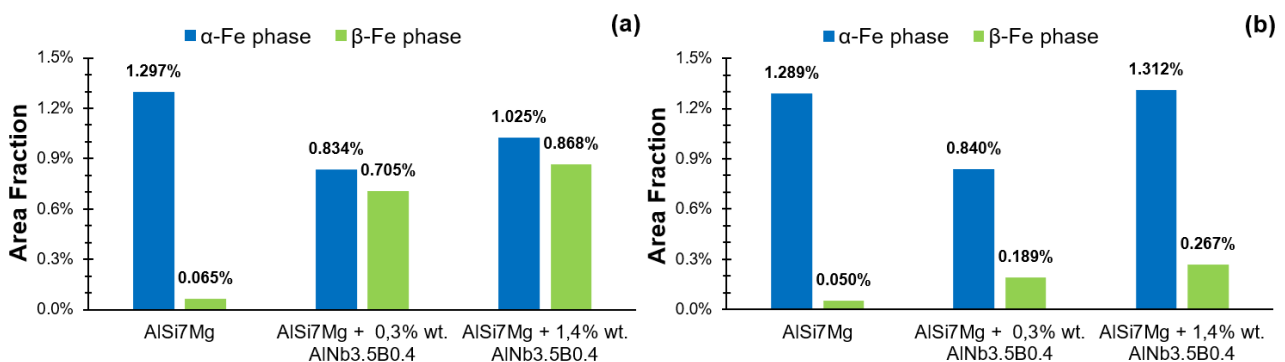

Figure 4 Area fraction of α-Fe and β-Fe particles in the whole Fe-rich compounds in the experimental alloys solidified at **(a)** higher and **(b)** lower cooling rate

Figure 5 shows the effect of AlNb3.5B0.4 grain refinement on the grain structure of AlSi7Mg alloy at different cooling rates. In general, the AlSi7Mg alloy shows coarser grains respect to grain refined AlSi7Mg alloys. Upon increasing the cooling rate from 0.1 to 1.3 °C/s, the average grain sizes moved from 2470±320 µm to 1650± 90 µm in the AlSi7Mg alloy. The additions of Nb-B inoculant progressively reduced the grain size. Regardless of the cooling rate, equiaxed grains with a size of 320±30 µm were obtained after 1.4 wt.% AlNb3.5B0.4 addition. These results are in agreement with the previous study of Bolzoni et al. [15], where it was demonstrated that Nb-rich compounds act like heterogeneous substrates for the refinement of Al-Si foundry alloy and make the final grain size less sensitive to the cooling rate.
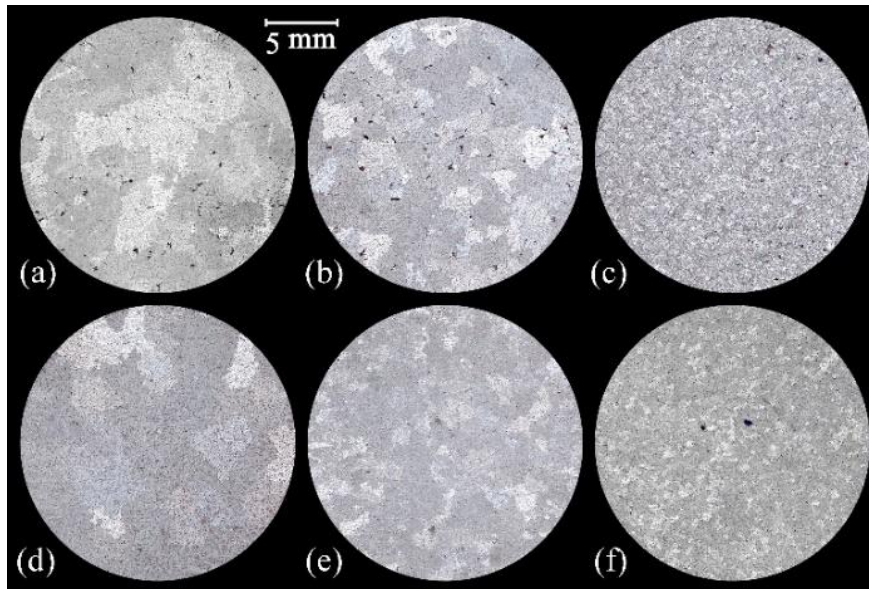
Figure 5 Grain structure of Al7SiMg alloy after **(a, d)** 0 wt%, **(b, e)** 0.3 wt% and **(c, f)** 1.4 wt% AlNb3.5B0.4 additions. The macrographs refer to different cooling rates during solidification: **(a-c)** 0.1 and **(d-f)** 1.3 °C/s.

4. CONCLUSION

In the present work, the influence of AlNb3.5B0.4 grain refinement on the precipitation of Fe-rich compounds was studied in a secondary AlSi7Mg alloy. The following conclusions can be drawn:

- The addition of AlNb3.5B0.4 grain refiner increases the density of polygonal Nb-rich particles in the microstructure.

- The precipitation of α-Fe and β-Fe compounds is largely affected by the cooling rate and the initial chemical composition of the alloy. The presence of Nb-B promotes the formation of β-Fe particles, especially at higher cooling rates.

- After AlNb3.5B0.4 grain refinement, the content of Nb-B does not significantly affect the size of the β-Fe particles, which appear finer at high cooling rates.

- The difference in grain size associated with the different cooling rates is suppressed after the addition of 1.4 wt% AlNb3.5B0.4.

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