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Grain refinement of Al–Si alloys by Nb–B inoculation. Part II: Application to commercial alloys

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ABSTRACT

The potency of Nb–B inoculation for the refinement of Al–Si cast alloy has been demonstrated in Part I of this work by the systematic analysis of binary Al–xSi alloys (where x = 1–10 wt.%). In Part II of this work the effect of Nb–B inoculation on commercial Al–Si alloys is assessed. Specifically, hypo-eutectic alloys such as LM24 (A380) and LM25 (A356) as well as near-eutectic LM6 (A413) Al–Si alloys are considered. The aim is to quantify the grain refinement and detect possible interaction with alloying elements commonly present in Al cast alloys, such as Mg, Fe, Cu, Mn and Zn. The in-depth analysis of the alloys solidified under wide range of cooling rates indicates that Nb–B inoculation does not only lead to a much finer microstructural features but also makes the final grain size far less sensitive to the cooling rate employed to solidify the material. Finally, the mechanism essential for the grain refinement of commercial Al cast alloys by Nb–B inoculation is determined on the base of SEM and thermal analysis results. It is found that in-situ formed Al_3Nb and NbB_2 intermetallic particles (forming from the interaction of Al alloy/Nb powder/KBF_4 flux) are the heterogeneous nuclei responsible for the grain refining of Al cast alloys.

1. Introduction

As discussed in Part I of this article, there is a great scientific interest in the development of efficient and reliable grain refiner for the Al industry because of the intrinsic advantages of finer microstructures [1–4]. Grain refinement is a common industrial practise for wrought Al [4–12] and it is mainly done by adding commercial master alloys. Modifications of the Al–Ti–B and Al–Ti–C master alloys have been recently investigated [13–17]. Commercial master alloys are not very effective on refining the most important Al casting alloys, i.e. the alloy based on the Al–Si system. The poor refinement is due to the interaction between Si and Ti which leads to the formation of titanium silicides depleting the melt of Ti. This phenomenon, which is called poisoning effect, is well known and was the subject of study of many researches [8,10,18–22]. Currently, the producers of Al cast part (e.g. automotive components manufacturers) do not use any grain refiner or employ the commercial Al–Ti–B master alloys even though of their poor performance. In Part I of this paper it has been demonstrated that Nb–B inoculation is able to refine the microstructural features, namely primary Al α-grains and Al–Si eutectic phase, of binary Al–xSi alloys (where x = 1–10 wt.%). Nevertheless, in that study the following aspects were not considered: (1) can Nb–B inoculation effectively refine commercial Al–Si alloys where other alloying elements, rather than Si, are present? (2) is there any effect from the cooling rate used in the different casting techniques, i.e. sand casting, permanent mould casting and high-pressure die casting after Nb–B inoculation? (3) what is the impact of the finer microstructure of commercial Al–Si alloy on their mechanical performances? and (4) what is the nature of the particles responsible for the grain refining by Nb–B inoculation? These questions arise because commercial Al casting alloys are based on the Al–Si system due to their high fluidity but their composition, normally, contemplate other alloying elements in order to fulfil specific requirements. For examples, copper (1.5–4.5 wt.%) increases strength and improves machinability, nickel (0.3–2.3 wt.%) improves elevated temperature properties and magnesium (0.1–1.3 wt.%) enhance the corrosion resistance [23]. Moreover, the different commercial Al–Si alloys were designed to be processed by diverse solidification techniques which, in turns, result in different cooling rates. This is also the case of casting products with complex geometry where different wall thicknesses of the same product solidify under different cooling conditions. The experimental work discussed in this work was designed to answer the questions previously listed and, therefore, the applicability of Nb–B inoculation was tested in commercial Al–Si alloys considering a great range of cooling rates. The effect of the grain refinement on the

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mechanical properties was determined as well. Finally, the attention was focused on the identification of the inoculants (potential heterogeneous nucleation substrates) responsible for the grain refinement of Al–Si alloys by Nb–B inoculation.

2. Experimental procedure

For the purpose of this study commercial hypo-eutectic and near-eutectic alloys were considered and their compositions are reported in Table 1.

From Table 1, the main difference between the two hypo-eutectic alloys, LM24 and LM25, is the amount of alloying elements added because LM24 has much higher content of Fe, Cu and Zn than LM25. The starting material was placed into a clay-bonded graphite crucible and melted at 800 °C in a conventional electrical resistance heating elements furnace. A dwell time of 1 h was set to guarantee the homogenisation of the temperature inside the molten metal. Afterwards, the reference alloy was left to cool down to 740 °C (±3 °C) and cast. In the case of the addition of the grain refiner, 0.1 wt.% of Nb powder (<45 μm) and KBF_4 flux were added to the melt (0.1 wt.%). The TP-1 test (Standard Test Procedure for Aluminum Alloy Grain Refiners) of the Aluminum Association [24] was used because it permits to determine the effect of the heterogeneous nucleation induced by the addition of grain refiners. Furthermore, in order to simulate the cooling rates of various casting techniques employed in the Al industry, a wedge-shaped copper mould was used. Finally, for the study of the undercooling by means of thermal analysis [6,25–28], the molten metal was left to cool inside an glass-wool externally lined crucible (cooling rate of ~0.3 °C/s). Once cast, the samples were cut and their cross-sections prepared for metallographic analysis by using the classical route of grinding with 120–1200 SiC papers plus polishing with OPS solution was employed. Macroetched cross-section samples were etched by means of Tucker's solution (15 ml HF + 15 ml HNO_3 + 45 ml HCl + 25 ml H_2O) whereas for microstructural analysis the specimens were electropolished. In particular, the samples were immersed into the electrolite (20 ml of perchloric acid ($HClO_4$) mixed with 80 ml of acetic acid) and a DC current of 30 V was applied during 2 min. The microstructural analysis was carried out with a Carl Zeiss Axioscope A1 optical microscope. The primary α-Al grain size and the Al–Si eutectic phase size were measured with the dedicated program from pictures taken at different position along the cross-section of the samples. Tensile samples were obtained by means of different techniques depending on the nature of the alloy. For the LM25 and LM6 alloys the tensile specimens were cast using a permanent steel mould and, afterwards, machined to specific dimensions (ASTM: E8). In the case of the LM24 and LM6 alloys, which have sufficiently high fluidity, tensile samples were obtained by means of the high pressure die casting (HPDC) method. Specifically, a LK® Machinery Co. Ltd. HPDC equipment with a diameter of the plunger of 60 mm, a maximum accelerating shot speed of 6.22 m/s and a maximum shot distance of 405 mm was used. The settings employed during the injection of the alloys were: die temperature of 180 °C, shot distance of 200 mm and trigger pressure of 70 bars. Tensile tests were performed on an Instron ® 5569 universal testing machine using a crosshead speed of 2 mm/min, equivalent to a strain rate of $1.33 \times 10^{-3}\ s^{-1}$. A 25 mm gauge length external extensometer was used to record the elongation of the samples. Ultimate tensile strength and strain at fracture (mean values of, at least, four tested samples) were obtained directly from the dedicated program of the universal testing machine. Vickers hardness measurements were performed by means of a Vickers-Armstrongs Ltd. Hardness tester.

3. Results and discussion

3.1. Effect of Nb–B inoculation and pouring temperature on the microstructure of commercial Al–Si alloys

The first experiment carried out was the comparison between the effect of the addition of the novel grain refiner and the commercial Al–5Ti–1B master alloy to the alloys solidified using the TP-1 mould (cooling rate approximately 3.5 °C/s) and employing three different pouring temperatures in each case. Specifically, for the LM24 alloy the pouring temperature ranges between 610 °C and 650 °C, for the LM25 from 630 °C to 680 °C whilst for the LM6 from 630 °C to 670 °C. Representative examples of micrographs are presented in Fig. 1 where, for brevity, the micrographs of each alloy with different addition (i.e. reference, Al–5Ti–1B and Nb–B) poured from one specific temperature are reported.

From the plane polarised light micrographs of the LM24 alloy without the addition of any grain refiner (reference), it can be seen that the microstructure is mainly composed of quite fine primary α-Al dendrites homogeneously distributed (Fig. 1a). With the increment of the pouring temperature from 610 °C to 650 °C, the size of the primary dendrites increases due to higher undercooling that the alloy experiences. The increment was quantified by image analysis and it was found that the primary Al α-grain size increases linearly approximately from 530 μm to 640 μm (Fig. 1j). In the case of the employment of a commercial Al–5Ti–1B master alloy (Fig. 1b), the main microconstituent of the LM24 alloy is still primary α-Al dendrites whose size increases linearly from 450 μm to 610 μm. Thus, the addition of the commercial Al–5Ti–1B master alloy has some grain refinement effect on the LM24 alloy but the benefits decreases with the increment of the pouring temperature. The average grain size reduction by the addition of the Al–5Ti–1B master alloy to the LM24 alloy is about 10 ± 5%. Finally, Nb–B inoculation leads to a further reduction of the primary α-Al dendrites in comparison to the commercial master alloy because the primary Al α-grain size ranges between 430 μm and 560 μm. Once again, there is an increment of the grain size of the LM24 alloy with the pouring temperature but this does not seem to be linear with the increment of the pouring temperature. After Nb–B inoculation (Fig. 1c), the LM24 alloy presents a grain size almost 18 ± 4% finer with respect to the reference material. The microconstituents of the LM25 alloy without any addition (reference) and poured at the lowest temperature considered (630 °C) are very fine primary α-Al dendrites of around 220 μm which gives the impression that the microstructure is composed of equiaxed grains (Fig. 1d). As in the case of the LM24 alloy, the increment of the pouring temperature leads to a significant increment of the size of the primary dendrites which reaches approximately 460 μm at 680 °C

Table 1
Chemical composition of the commercial Al–Si alloys considered in the study.

Alloy type	Element (wt.%)								
	Al	Si	Mg	Fe	Cu	Mn	Ni	Zn	Ti
LM24 (A380)	Bal.	8.5	0.13	1.2	3.37	0.19	0.04	1.36	0.04
LM25 (A356)	Bal.	6–8	0.3	0.5	0.003	0.005	–	0.003	0.11
LM6 (A413)	Bal.	10.0–11.0	0.3	0.6	0.01	0.5	0.1	0.1	0.1