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Grain refinement of Al–Si alloys by Nb–B inoculation. Part I: Concept development and effect on binary alloys

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ABSTRACT

The effect of Nb–B inoculation on Al–Si alloys for their grain refinement has been studied through the analysis of binary Al–xSi (where x = 1–10 wt.%) to avoid possible effects of other alloying elements. In Part I of this work the concept development of the Nb–B inoculation is discussed in detail on the basis of the theoretical and fundamental concepts employed (i.e. pro-peritectic particles formation, lattice structures and mismatch as well as analogies between the Al–Ti/Al–Nb or Ti–Si/Nb–Si binary phase diagrams). The systematic study of the addition of different level of Nb–B inoculation to pure Al permitted to determine the best addition rate. From the microstructural and thermal analysis of binary Al–xSi alloys it is found that Nb–B inoculation is highly suitable for Al–Si alloy with Si content greater than 6 wt.%. As results of the Nb–B inoculation the microstructural features of binary Al–xSi alloys (i.e. primary Al α-grains and eutectic phase) are significantly refined. Most importantly, the inoculation of Al–Si cast alloys with Nb–B is not characterised by any visible poisoning effect (i.e. formation of silicides) which is the drawback of using commercial Al–Ti–B master alloys on Al cast alloys. The effect of Nb–B inoculation on commercial Al–Si alloys (which normally include other alloying elements in their chemical composition) is assessed in Part II of this work.

1. Introduction

Aluminium and its alloys are common engineering materials for structural applications due to the combination of properties they can provide. Specifically: low density (2.7 g/cm^3), corrosion resistance in many environments, good specific strength (i.e. strength to density ratio), good thermal conductivity and low electrical resistivity. As for other metals, the primary process employed to fabricate Al alloys is used to differentiate and categorise them as wrought and cast. Cast Al alloys are based on the binary Al–Si phase diagram and are used because of their low melting point, good fluidity, good surface finishing as well as limited solubility for gases (except for hydrogen). Other alloying elements such as magnesium and copper are generally contemplated in the alloy composition to achieve specific properties like improved corrosion resistance or better response to heat-treatments. Depending on the production route employed, Al can be characterised by quite coarse microstructure and, thus, its grain refinement it is a common industrial practise [1]. Usually, the grain refinement is carried out by the addition of commercial master alloy developed and based on the ternary Al–Ti–B system, such as the Al–5Ti–1B master alloy, which is added to the melt prior casting [2–5]. It is worth mentioning that Ti is the elements with the highest growth restriction factor [6], which plays an important role in the refinement of Al by means heterogeneous nucleation. The mechanism behind the grain refinement of Al has been a topic of debate and various theories were proposed: phase diagram/peritectic theory, peritectic hulk theory, hypernucleation theory, and solute theory [7–9]. Summarising, the employment of commercial Al–Ti–B master alloy is based on the scientific fundamental that Ti reacts with B forming TiB_2 particles and with Al forming Al_3Ti intermetallic particles. When the commercial master alloy is added to the molten Al, TiB_2 particles act as heterogeneous nucleation sites whilst Al_3Ti intermetallics dissolve into the melt on the base of the peritectic reaction forming α-Al: liquid $Al + Al_3Ti \rightarrow \alpha\text{-}Al$ (solid solution) [9,10]. Observation of the interface Al_3Ti layer on TiB_2 particles suggested that TiB_2 particles in combination with Al_3Ti contribute to the heterogeneous nucleation of α-Al grains [11]. Commercial Al–Ti–B master alloy are very potent grain refiners for wrought Al alloys, whose Si content is generally lower than 2 wt.%. Nonetheless, in the case of cast Al alloys, where Si content is greater than 4 wt.%, the efficiency of commercial Al–Ti–B master alloys is relatively poor. This is due to the interaction of Ti with Si to form titanium silicides (i.e. TiSi, $TiSi_2$ and Ti_5Si_3) which depletes the melt

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of Ti preventing the grain refinement of the alloy. This phenomenon has been the subject of different studies and it is known as poisoning effect [4,12–14]. Many attempts and a lot of effort have been focused in achieving fine equiaxed grain structure in as-cast Al–Si alloys by the addition of small quantities of elements called hardeners (which includes Zr, Nb, V, W, Ta, Ce, etc. [15–19]) but without much success. The latest works focused on the effect of commercial Al–B master alloys (i.e. Al–3B), Al–Ti–C master alloys [20], Al–Ti–B–C master alloys [21] or variants of the Al–Ti–B master alloys [22,23]. The most significant result of research done by Birol [24] is that the Al–3B master alloy performs very well in refining Al–Si alloys grain structure when they are Ti-free, which is not the case for most of the Al cast alloys. When Ti is present as impurity in percentage greater than 0.04 wt.% the Al–3B master alloy refining potency is equal to that of commercial master alloys based on the Al–Ti–B ternary system (i.e. Al–5Ti–1B and Al–3Ti–3B) [24]. Potential heterogeneous nucleation substrates for grain refinement have to be characterised by three main aspects [25]: (1) high melting temperature to prevent their melting when placed in contact with the molten metal to be refined, (2) low lattice mismatch with the nucleating phase and (3) chemically stability (do not interact with the alloying elements). The aim of this work is to report and discuss the grain refinement of Al–Si cast alloys by Nb–B inoculation, chemical composition which was patented [26,27]. In particular, the concept development and the effect of Nb–B inoculation in binary Al–*x*Si alloys (where x = 1–10 wt.%) are discussed in Part I. Binary Al–Si alloys were chosen because they permitted to quantify the effect of Nb–B inoculation on the microstructural features (primary α-Al dendrites and secondary eutectic phase) without the concern of possible side effects of other alloying elements present in commercial Al–Si cast alloys. The effect of the addition of the Nb–B grain refiner to commercial Al–Si cast alloys solidified over a great range of cooling rates as well as the mechanism governing their grain refinement are assessed in Part II of this work.

2. Experimental procedure

The work described in this paper is divided into three main sections, namely (1) the study of the addition of Nb to commercial pure Al, (2) the study of the addition of interstitials (B and C) to the Al–Nb system and (3) the study of the addition of the 0.1Nb–0.1B to Al–*x*Si binary alloys. Therefore, at each specific time different materials and methods were used. Nevertheless, the general path followed is reported in this section and it is applicable for the experiments described unless otherwise specified. The raw materials employed were:

- Commercial pure Al (Al > 99.5 wt.%, Si = 0.02 wt.%, Fe = 0.08 wt.%, Mn = 0.01 wt.%, Zn = 0.02 wt.%, Ti = 0.06 wt.% and Ga = 0.05 wt.%) supplied by Norton Aluminium: used to test the refining potency of Nb and Nb–B as well as for the production of binary Al–*x*Si alloys, where x = 1–10 wt.%.
- Al–50Si master alloy: mixed with pure Al to produce binary Al–*x*Si alloys, where x = 1–10 wt.%. The Al–*x*Si alloys were produced in batches of 5 kg and their chemical composition was checked by means of an appositely calibrated FOUNDRY-MASTER Pro equipment (Oxford Instruments).
- Nb powders (Nb > 99.8%) with big particle size (average particle size 100 μm) and with fine particle size (lower than 45 μm) procured from Alfa Aesar. Initially (Section 3.1.2) the coarse Nb powder was used and it was found that it shows poor dissolution into Al although it permitted to study the sedimentation of Nb particles. Subsequently (from Section 3.1.3 onwards) all the experiments were carried out using the fine Nb powder. The total amount of Nb added varied during the development of the composition of the novel Nb–B grain refiner (Fig. 6) but it was then set to 0.1 wt.% (targeted addition) during the study of its performances on Al–*x*Si alloys.
- B powder (B > 98%) with particle size lower than 45 μm: initially used to study the combined effect of Nb and B on pure Al (Section 3.2.2). Lately (from Section 3.2.3 onwards), switched the potassium tetrafluoroborate (KBF_4) due to the non-wetting behaviour of the B powder which hinders its dissolution into the melt. Once again, the amount of B added to the melt was changed during the initial experiment (Fig. 6) but then fixed at 0.1. wt.% (targeted addition) during the study of the performances of Nb–B inoculation. It is worth mentioning that, although 0.1 wt.% was targeted, the actual content of Nb–B, measured by ICP method, is lower due to partial oxidation of the Nb powder during addition to the melt, low B recovery from KBF_4 and non-optimised mixing process.
- Potassium tetrafluoroborate (KBF_4 > 98%) flux purchased from Alfa Aesar: employed as alternative source of B.
- Graphite powder with particle size lower than 20 μm: employed to study the combined effect of Nb and C on pure Al.
- Commercial Al–5Ti–1B master alloy supplied by London & Scandinavian Metallurgical Co Limited: used to compare the performance and efficiency of Nb–B inoculation. The amount of master alloy added was equal to 0.1 wt.% which is a common percentage employed at industrial level.

Pure Al and binary Al–*x*Si alloys (where x = 1–10 wt.%) were melted and/or prepared in clay-bonded graphite crucibles and maintained at temperature for, at least, one hour. The melting temperature changed depending on the type of experiment (i.e. production of the binary Al–*x*Si alloy or grain refinement) and it varied between 720 °C and 800 °C. Specifically, 800 °C was mainly used when the addition of the Nb–B inoculant was considered. In the case of the pouring temperature, this parameter ranges between 660 °C and 720 °C depending on the nature of the experiments (i.e. study of the influence of the casting temperature). In some cases (e.g. study of the effect of the refiner on the base of the thermal analysis) the melt was left to cool inside a crucible externally lined with a glass wool insulator which permitted a very slow cooling rate (i.e. ~0.3 °C/s). The cast samples were prepared for metallographic analysis by using the classical route. In the case of macroanalysis, samples were grinded and etched by means of Tuckers' reagent whereas for microstructural analysis the samples were fine polished with OPS and characterised by means of an optical microscope (Carl Zeiss Axioscope A1) and/or SEM (Zeiss Supra 35VP FEG). The TP-1 test (Standard Test Procedure for Aluminum Alloy Grain Refiners) of The Aluminium Association [28] was used to compare the grain refinement efficiency because it permits to maintain a constant cooling rate and to determine the effect of the heterogeneous nucleation induced by the addition of grain refiners (cooling rate is ~3.5 °C/s). Grain size measurements were carried out on the base of the intercept method as per ASTM: E112. Cooling curves from liquid to solid of the selected composition were measured with K-type thermocouples and recorded by means of dedicated software (NI-VI Logger) collecting 100 data per second.

3. Results and discussion

3.1. Study of the addition of Nb to commercial pure Al

3.1.1. Analogies/differences between the Al–Ti and Al–Nb binary systems

Nb is a promising candidate for the refinement of Al and its alloys because, like Ti, it is characterised by a peritectic reaction