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Original Article

Towards industrial Al-Nb-B master alloys for grain refining Al-Si alloys

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ABSTRACT

It has long been known that foundry Al-Si alloys cannot reliably and consistently be grain refined by means of Ti-containing master alloys due to reaction between Ti and Si. Over the last years we developed and studied new Nb-based grain refiners consistently demonstrating the effectiveness of Nb + B inoculation on foundry alloys studying various Al-Si compositions solidified under different cooling conditions. Most of our studies focused on achieving the finest possible grain size using a lab made Al-2Nb-2B master alloy. This work presents the results, issues, and advancements made from the early stages of development to the first pilot scale trial. Moreover, the results of the present study are a further justification of the choice of the Al-2Nb-2B *nominal* composition, which was primarily dictated by the poor yield/recovery of Nb and B from their raw materials at lab scale. In the present work, emphasis is put on addressing the unanswered question about the effect of Nb to B ratio considering the inoculation of an Al-10Si alloys via the addition of Al-Nb-B master alloys with different stoichiometries.

1. Introduction

Ti-containing master alloys (e.g., Al-5Ti-1B, compositions are in wt.% if not otherwise indicated) are the most extensively industrially used and scientifically studied materials for the grain refinement of Al alloys via chemical inoculation. This is because of the benefits associated with having a fine equiaxed grain structure, which include higher mechanical properties, lower and smaller shrinkage porosity (i.e., lower rejection rate due to the improved soundness of the castings), and reduced hot tearing susceptibility [1–3]. Furthermore, a fine grained cast material has a more isotropic response to downstream processes such as cold/hot deformation and heat treatments. Since the early day of solidification science, different aspects related to understanding the performance and the mechanism of these Ti-containing master alloys have been thoroughly studied. Examples include studies of the relative effect of solute and nucleant [4], the effect of the size distribution of inoculant particles [5], and modelling of the inoculation efficiency [6]. Therefore, the optimisation of these commercial Ti-containing master alloys is continuing over more than 60 years and is still a very much active field of research as recent literature confirms [7–9].

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From early studies onwards it has been repeatedly shown that Ti-containing master alloys are not as effective (i.e., limited grain refinement capability) and reliable (i.e., not consistent from study to study or batch to batch and subjected to fast fading of their efficacy) on foundry Al-Si alloys. The main reason is the reactivity of Ti with Si that leads to the formation of Ti silicides where this phenomenon is known as poisoning and has also been thoroughly studied [10–13]. Ti silicides have greater lattice mismatch with the Al lattice in comparison to TiB_2/Al_3Ti and thus cannot efficiently promote the heterogeneous nucleation of new grains. As per the classical nucleation theory, a low lattice mismatch is needed to minimise the barrier to nucleation. Thermodynamics modelling and simulations have also indicated that the interaction between Ti and Si changes the nature of the first phase that actually nucleates upon cooling. Moreover, excess Ti increases the growth rate of Al-dendrites so that growth wins over nucleation [14–17].

Even though of these early scientific evidences, different studies were and are still performed on the addition of Ti-containing master alloys to foundry Al-Si alloys. Examples are studies on the effect of stoichiometric (i.e., Ti:B = 2.2) or sub-stoichiometric Al-Ti-B compositions or the replacement of B with C (e.g., Al-Ti-C). However, as Ti is the critical element, intrinsically no much improvement could be achieved. Other authors have proposed the use of Ti-free grain refiners like Al-B master alloys, where Al borides (e.g., AlB_2 and AlB_{12}) are the heterogeneous substrates added to the molten alloy. Borides seem to be quite effective if the foundry Al-Si alloys is also Ti-free [18,19]. However, this approach is industrially challenging as the great majority of foundry alloys already contain Ti (approx. 0.1%) regardless whether it is present as an impurity or it was purposely added. When Al-B master alloys are used to inoculate Ti-containing foundry Al-Si alloys, their efficiency is comparable to that of Al-Ti-B master alloys [18,19]. This is due to the fact that TiB_2 is much more thermodynamically stable and therefore the Al borides of the Al-B master alloys transform into Ti borides, which are subjected to poisoning.

We previously demonstrated that Nb + B inoculation is highly effective for the refinement of commercial hypoeutectic [20] and near-eutectic/eutectic [21,22] Al-Si alloys, and it can prevent the formation of columnar grains in directionally solidified Al-Si alloys [23]. From early studies about the development of a potential new grain refiner for foundry Al-Si alloys, it was found that the recovery of B from KBF_4 was quite poor at lab scale. Therefore the use an Al-5B master alloy for the addition of B, which helped to improve the recovery rate, was contemplated. The yield of Nb recovery from powder was also found to be quite low and variable as Nb easily oxidises at high temperatures. Because of these aspects and the fact that in the early studies our effort was purely focused on achieving the smallest grain size possible as to demonstrate the efficiency of Nb + B inoculation, most of the published studies were performed using an Al-2Nb-2B master alloy with already improved yield of recovery [20,22,23]. However, it has to be specified that the actual composition of the master alloys is lower than the theoretical 2% of Nb and 2% of B because of recovery/oxidation related issues. That is why compositions and addition rates are generally reported as "*nominal*". Although of previous publications, to date the effect of varying the Nb to B ratio on the grain refinement of Al-Si alloys via Nb + B inoculation is still uncertain.

The current work aims to validate Al-Nb-B master alloys as alternative for the grain refinement of foundry Al-Si alloys. For that this manuscript mainly presents three stages of development. Firstly, in the "Lab scale Al-Nb-B master alloys produced with KBF_4" section, the initial lab scale experiments, where a broad range of Nb to B ratios were studied, are discussed. This is done to highlight the issues encountered and justify the need to investigate the manufacturing of lab scale Al-Nb-B master alloys with Nb to B ratio equal (i.e., B = Nb) or higher than 1 (i.e., B < Nb). Thus the grain refinement results obtained using lab scale Al-Nb-B master alloys produced via an improved methodology are analysed in the "Lab scale Al-Nb-B master alloys produced with Al-5B" section. These results served as guide for the preliminary industrial development. Finally, results obtained using Al-Nb-B master alloys manufactured at industrial scale in a pilot implant are presented in the "Industrial pilot scale Al-Nb-B master alloys produced with KBF_4" section. The full development of Al-Nb-B master alloys presented helps to clarify the unanswered question about the effect of Nb to B ratio as all the grain refining experiments were preformed using the same experimental conditions.

2. Experimental procedure

The development of Al-Nb-B master alloys discussed in this manuscript has three main sub-sections as at least one key aspect was significantly changed from one to the other. The procedure henceforward described is common for all the experiments performed unless otherwise discussed. The first two sub-sections deal with experiments where the Al-Nb-B master alloys were produced at lab scale. The key improvement among the two is the use of an Al-5B master alloy rather than KBF_4 as a source of B combined with a simultaneous enhancement of the preparation method to prevent the oxidation of Nb during its addition to the molten Al put in place. It is worth mentioning that although of the precautions taken and the improvement in the production method, the actual content of both Nb and B is lower than the *nominal* values due to lab scale related processing limitations. These limitations include, for example, the maximum temperature, which, in turns, determines the solubility of Nb in Al. Finally, the third sub-section deals with Al-Nb-B master alloys produced in an industrial pilot scale where 50 kg of each master alloy were manufactured. It is worth mentioning that at least three replicas for each inoculation experiments were performed.

Interested readers can find a detailed analysis of the type of inoculants (Al_3Nb and NbB_2), their crystal structure (i.e., tetragonal and hexagonal, respectively), their lattice constant, their particle size distribution (approx. 0.5–10 μm for lab made master alloys), as well as interfaces and orientation relationship to promote the heterogeneous nucleation of α-Al grains in ref. [20,23–27].

2.1. Lab scale Al-Nb-B master alloys produced with KBF_4

The raw materials for the initial fabrication of the Al-Nb-B master alloys are: (1) commercially pure Al with purity higher than 99.5% purchased from Norton Aluminium Ltd., (2) Nb powder with maximum particle size lower than 45 μm and purity greater than 99.8%, and (3) potassium tetrafluoroborate (KBF_4 >98%) flux purchased from Alfa Aesar. Once Al was melted, KBF_4 and Nb were simultaneously added at 850 °C and left to dissolve during 2 h with intermediate manual stirring. The melt was then cooled down to approx. 700 °C and cast into small ingots, as per our first report on the production of Al-Nb-B master alloys [26]. For this set of Al-Nb-B master alloys a broad range of Nb to B ratios (i.e., <1, =1 and >1) were investigated with the aim to identify the most promising compositions.

2.2. Lab scale Al-Nb-B master alloys produced with Al-5B

To improve the yield of recovery of B, an Al-5B master alloy supplied by LSM Co. Ltd was added to the molten Al and left to dissolve at 850 °C/1 h. Subsequently, the correct amount of Nb powder wrapped into Al foil was carefully submerged into the melt to limit oxidation of the powder. The melt was left at maximum temperature during three hours performing manual stirring every 15′ with the aim of effectively dissolve Nb [20,22]. The melt was furnace cooled down to 700 °C and finally stirred until solid rather than cast to prevent sedimentation of the Nb-based particles. Through this procedure only Al-Nb-B master alloys with a fixed *nominal* amount of 2% Nb combined with two additions of B were manufactured. Specifically, compositions with *nominal* Nb to B ratios of 2:1 and 2:2 were considered on the basis of the results obtained in the first part of the study (i.e., Lab scale Al-Nb-B master alloys produced with KBF_4). Furthermore, in an attempt to increase the efficiency, a master alloys with a *nominal* composition of Al-5Nb-5B was also fabricated.

2.3. Industrial pilot scale Al-Nb-B master alloys produced with KBF_4

On the basis of previous results, the manufacturing of the Al-Nb-B master alloys in an industrial pilot scale focused on manufacturing batches of 50 kg of master alloys with 2% Nb and 1% B was considred. An in-house made Al-10Nb master alloy and KBF_4 to produce 10 kg waffles using a comparable route (i.e., temperatures, mixing, etc.) to the one industrially used to manufacture Al-Ti-B master alloys was used. As per the standard industrial route, the Al-Nb-B master alloy waffles were cast.

2.4. Inoculation experiments

Grain refinement experiments were done using an Al-10Si alloy (actual composition 9.9%Si and 0.09%Fe) conventionally used to produce DC (Direct Chilled) casting billets. Batches of the alloy were melted inside clay bonded graphite crucibles at 790 °C/1 h and cast at 740 ± 3 °C. Inoculation of the Al-10Si alloy with the Al-Nb-B master alloys was performed while the melt was at 790 °C keeping a consistent contact time of 30′ and *nominal* addition rate equivalent to 0.1%Nb. The cast samples were sliced in two halves. One was used for visual analysis by means of grinding plus macroetching using Tucker's reagent. The other was used for microstructural analysis where the preparation was done via the traditional metallographic route. Moreover, for grain size measurements, which were done as per the intercept method (ASTM E112) using a Zeiss Axioscope microscope, the polished samples were anodised using a H_2O-based HBF_4 solution.

3. Results and discussion

3.1. Lab scale Al-Nb-B master alloys produced with KBF_4

Fig. 1 shows representative micrographs of the polished/anodised Al-10Si samples without and with Nb + B inoculation. The microstructure of the reference Al-10Si is composed of coarse primary α-Al dendrite (2980 ± 200 μm), coarse needle-like secondary eutectic phase (length of the needles approx 70–80 μm), and primary Si particles 20–50 μm in size. The distribution of the eutectic phase is rather heterogeneous and mainly confined in between the dendritic arms of the growing grains. After the addition of Al-Nb-B master alloys, the size of primary α-Al grains is significantly reduced, there is a uniform distribution of principally fine eutectic needles (5–10 μm) with some few long particles (30–40 μm), and only few primary Si particles (5–10 μm).

It is worth mentioning that the absolute effect of Al-Nb-B master alloys on the final grain size significantly depends on the chemistry of the master alloy as well as the addition level employed. The histograms reported in Fig. 2 present the variation of the grain size for master alloys with fixed *nominal* Nb to B ratio. The level of Nb can be adjusted depending on the grain size acceptance level. However, a minimum *nominal* addition of 0.05% has to be used to reduce the size of the primary α-Al dendrites below 1000 μm (Fig. 2b). The comparison of the master alloys with Nb = B seems to indicate that a higher level of Nb is beneficial, potentially due to greater number of Nb-based compounds present in the master alloy. It is clear that low B master alloys (i.e., B < Nb) performs better than the other Al-Nb-B master alloys, especially in comparison to those with high B content. This is because in the case of master alloy with low B, it is more likely to form NbB_2 compounds (it has been reported that the stability range for NbB_x is $x = 1.86–2.34$ [28]) and Al_3Nb. Conversely, in the case of high B master alloy, there is a higher chance of having a great number of AlB_y compounds, where $y = 2–12$.

The increment of the Nb content is expected to reach the supersaturating concentration of Nb and, thus, the variation of the grain size is supposed to follow a powder-law (Eq. 1), which is shown in Fig. 3:

$$d = K\cdot(Nb)^{-n} \tag{1}$$

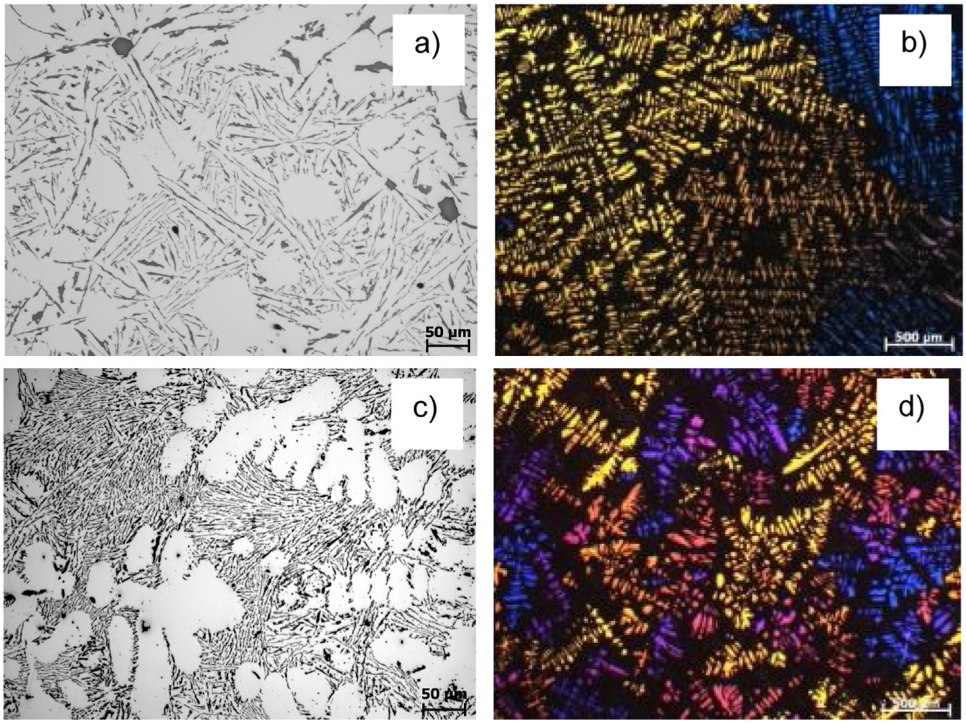

Fig. 1 – Optical/polarised light micrographs, respectively, for the Al-10Si alloy: a) and b) reference, and c) and d) inoculated with Al-Nb-B master alloys.

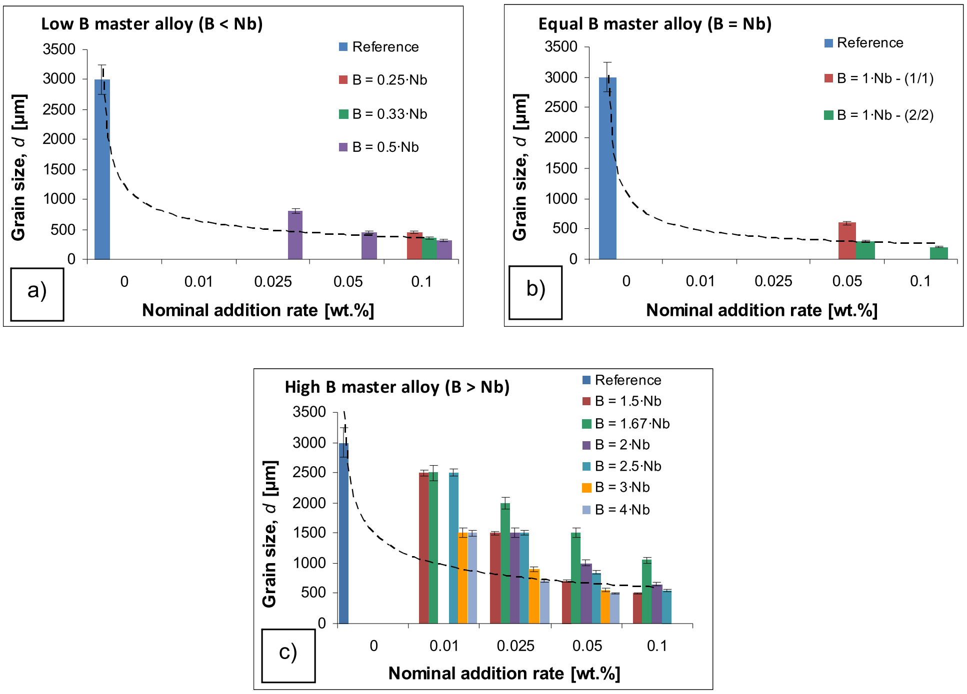

Fig. 2 – Variation of the grain size (*d*) vs. *nominal* Nb addition for different lab made Al-Nb-B master alloys: a) B < Nb, b) B = Nb, and c) B > Nb.

K and *n* are fitting parameters that vary with the *nominal* amount of Nb in the Al-Nb-B master alloys, the Nb to B ratio, and the level of addition of master alloy.

The powder-law equations of the different cases were used to simulate the variation of the grain size, which confirms that the higher the addition rate the finer the grain size (Fig. 3a). Al-Nb-B master alloys with B < Nb or B = Nb show quite comparable performance and the master alloy with B > Nb have poorer refining efficiency. The plotting of the data versus the B concentration (Fig. 3b) indicates that the best performances

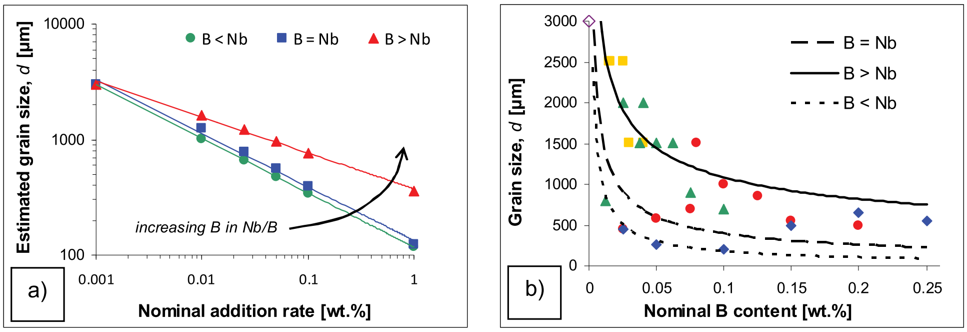

Fig. 3 – Variation of the grain size (*d*) after inoculation with different lab made Al-Nb-B master alloys: a) estimation of the grain size as per Eq. (1), and b) *d* versus B content.

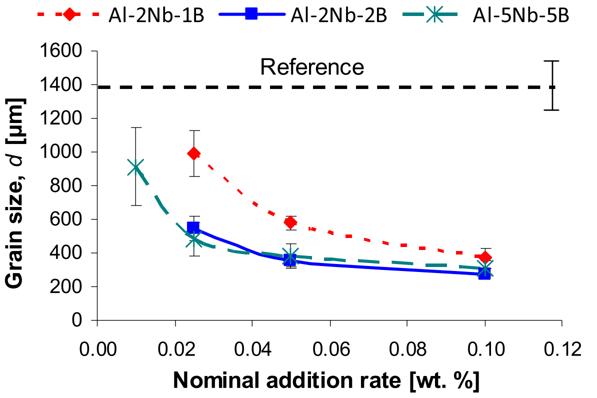

Fig. 4 – Variation of the grain size (*d*) vs. *nominal* addition rate for lab scale manufactured Al-Nb-B master alloys.

with the lowest *nominal* addition rates are obtained with master alloys with B < Nb.

3.2. *Lab scale Al-Nb-B master alloys produced with Al-5B*

The first set of experiments permitted to realise that, at lab scale, the yields of recovery of both Nb and B were very poor (in the order of 1–4% of the *nominal* value) and indicated that Al-Nb-B master alloys with *nominal* 2% Nb were promising and worth further investigation. Therefore, master alloys with *nominal* Al-2Nb-1B and Al-2Nb-2B composition were manufactured with an improved process achieving a yield of recovery of approx. 60% for Nb and > than 30% for B. The same process was also used to fabricate an Al-5Nb-5B seeking to be able to reduce the master alloy *nominal* addition rate. It is worth mentioning that the yield of Nb recovery, especially for the 5 wt.% Nb master alloy, is however expected to be low as the liquidus temperature of binary Al-Nb alloys raises significantly for small additions of Nb as per the Al-Nb phase diagram and the master alloys were produced at 850 °C.

The variation of the grain size of the Al-10Si alloy inoculated with different addition level shown in Fig. 4 confirms that the grain size decreases with the addition level (i.e., *nominal* amount of Nb added) regardless of the type of Al-Nb-B master alloy used. It is worth noticing that the reference alloy has smaller grain size with respect to that of Figs. 1 and 2 (i.e., 2980 µm) due to the different cooling rate used in the experiments. The Al-2Nb-2B and Al-5Nb-5B have comparable efficacy but Al-2Nb-2B is slightly better than Al-5Nb-5B at higher *nominal* addition rates. This indicates that the efficiency of the master alloy cannot be improved by increasing the content of Nb in the master alloy, at least with the lab scale production method used. A higher amount of Nb and B in the master alloys was expected to lead to the formation of more Nb-based compounds. The hypothesis tested was that for an equivalent *nominal* Nb content, the Al-5Nb-5B master alloy would have a greater number of potential heterogeneous nucleation substrates permitting to obtain finer grain size with lower addition rates.

As the grain refinement via chemical inoculation is determined by the nature and features of the heterogeneous nucleation sites and the solute, microstructural analysis of the master alloys was performed in order to justify the results shown in Fig. 4. The microstructure of the Al-2Nb-2B master alloy, which is also representative of the Al-2Nb-1B, has a quite uniform distribution of Nb-based compounds (i.e., NbB_2 and Al_3Nb) embedded into the Al matrix (Fig. 5a and c). Some few B-rich particles (i.e., AlB_x) are also present. For the Al-5Nb-5B, Nb-based compounds were formed from the reaction of Nb with Al and the Al-5B master alloy but a significantly number of coarse Al borides and undissolved Nb particles are still present (Fig. 5b and d). This indicate that the processing parameters used to manufacture this master alloy at lab scale are not optimised. From the Al-Nb phase diagram [29], the melting temperature of binary Al-Nb alloys steeply increases with the amount of Nb dissolved into Al. Therefore the temperature used was not high enough the fully dissolve the *nominal* amount of 5% Nb. As not enough Nb is dissolved, the transformation of Al borides to Nb borides is slowed down and hindered, and consequently longer time at temperature would be needed although the process will always be held back by the amount of Nb reacted. It is worth noticing that the two master alloys were manufactured using the same process and have the same grain refining efficiency (Fig. 4). From the free growth model [6] it is inferred that they would have similar amount of Nb-based compounds with comparable features. Specifically, the inoculating particles are expected to have similar morphology and particle size distribution as these particles are the ones that actually trigger nucleation events [23].

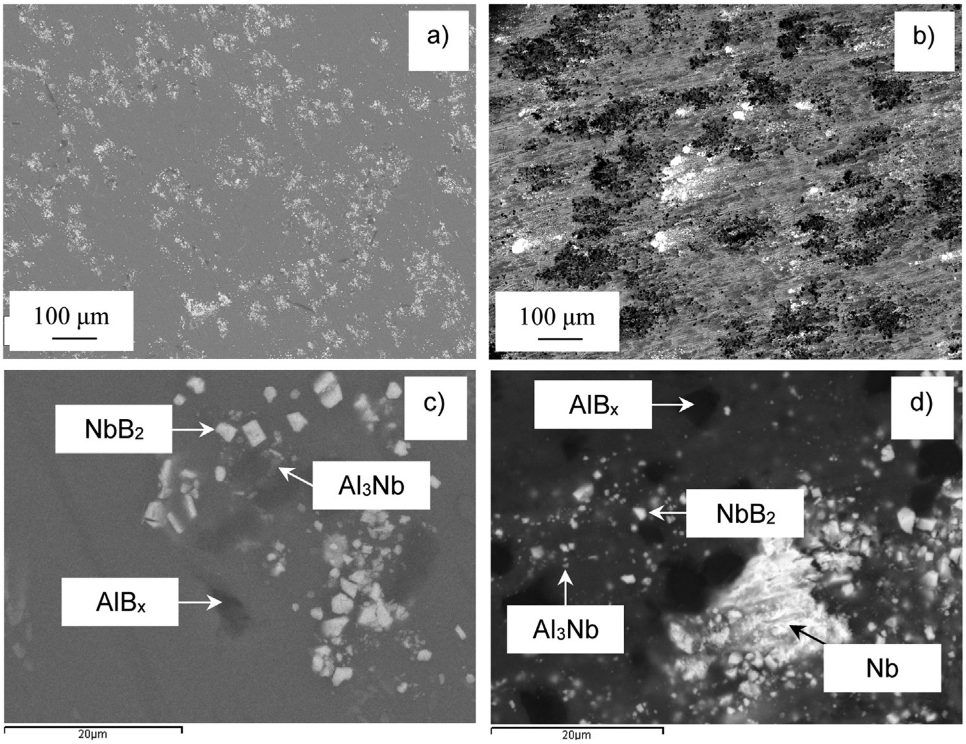

Fig. 5 – SEM micrographs of the microstructure (a and b) and details of the phases (c and d) found the in Al-2Nb-2B and Al-5Nb-5B master alloys, respectively.

3.3. *Industrial pilot scale Al-Nb-B master alloys produced with KBF_4*

The scientific and technical knowledge acquired from the experiments performed about the manufacturing of the master alloys at lab scale and their grain refining performances [20,23–27] served for planning the manufacturing of the Al-Nb-B master alloys at industrial pilot scale. It was decided to run two manufacturing trials but the *nominal* composition of the master alloy was fixed at 2% Nb and 1% B on the basis of the expectation that a higher recovery rate of B from KBF_4 is usually achieved at industrial scale. The industrially produced master alloys were subsequently tested by inoculating the Al-10Si alloy and the results are shown in Fig. 6. This set of experiments further validated the grain refining ability of Al-Nb-B master alloys in Al-Si cast alloys. In particular, the grain size of the inoculated alloy is always smaller than that of the reference material. The grain size proportionally decreases with the *nominal* addition rate. However, it was found that these first pilot scale mater alloys (i.e., MA1 and MA2) are not as good as the lab made master alloys, especially at the lower addition rates and therefore further improvement of their industrial production is needed.

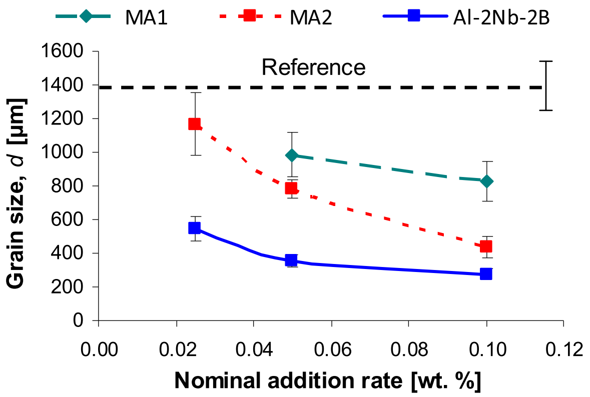

Fig. 6 – Variation of the grain size (*d*) vs. *nominal* addition rate for industrial pilot scale manufactured Al-2Nb-1B master alloys in comparison to the lab made Al-2Nb-2B master alloy.

Microstructural analysis of the pilot scale master alloys was performed to gain a better understanding of their performances and the results are presented in Fig. 7. Due to the different conditions used in the production trials (e.g., temperature, holding time, etc.), the amount and distribution of the particles present in the master alloys are significantly different. MA1 is characterised by a slight uneven distribution of particles embedded into the Al matrix. The great majority of these particles are Al borides derived by the reaction of Al with KBF_4 and very few Nb-based compounds are present. This indicate that the manufacturing conditions used are not ideal. In thermodynamics terms AlB_y are less stable with respect to NbB_x and should have therefore been transformed into Nb borides (provided that Nb could be effectively dissolved into Al). Moreover, it was also found that the process used did not guarantee a high cleanness of the master alloy as residue of the use of KBF_4 were found. Conversely, no such type of residue were present in MA2, which has a much more

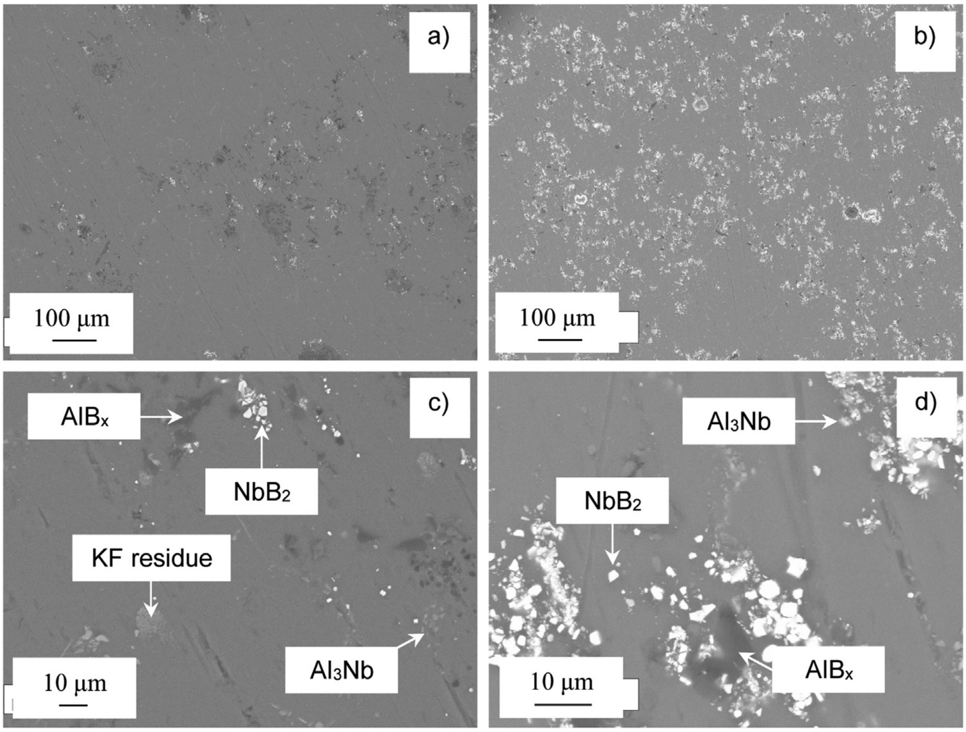

Fig. 7 – SEM micrographs of the microstructure (a and b) and details of the phases (c and d) found the MA1 and MA2 industrial pilot scale Al-2Nb-1B master alloys, respectively.

uniform distribution of particles. Most of these particles are actually Nb-based compounds although some Al borides are also present.

The microstructural results shown in Fig. 7 are consistent with the variation of the grain size. The grain refining ability of MA1 is poorer than that of MA2 even though both of them are not comparable to the lab made Al-2Nb-2B master alloy (Fig. 6). This is due to the different nature, relative amount, and particle size distribution of the particles present in each master alloy. The process used to make the master alloys at lab scale leads to the formation of a greater number of more suitable Nb-based compounds for the nucleation of primary α-Al grains. A final remark should be made about the grain refining performance of MA1 as it is mainly composed of Al borides. Consistently with recent literature on the subject [18,19,30–32], this set of experiments seems to confirm that Al borides have the ability of refining the grain size of Ti-free Al-Si alloys, which is the case of the Al-10Si alloy used in this study.

4. Conclusions

From this study about the validation of Al-Nb-B master alloys as effective candidates for refining the grain size of Al-Si cast alloys the following conclusions can be drawn:

- Independently of all the variables studied including lab/pilot scale production, yield of recovery and *nominal* addition rate, the grain size of the Al-Si alloys inoculated with Al-Nb-B master alloys is always finer in comparison to non-inoculated alloys (i.e. reference alloy solidified using a range of casting parameters);
- The manufacturing route, the processing parameters, and the nature of the raw materials used have a huge impact on the yield of recovery of both Nb and B and thus on the quality and efficiency of the Al-Nb-B master alloys. Each aspect affects the nature, distribution, and size of the particles that will act as heterogeneous nucleation sites for primary α-Al grains;
- As the grain size decreases exponentially with the *nominal* addition rate, optimisation and improvement of the manufacturing route should be done. This would be especially important for the industrially produced master alloys as their efficiency is still not comparable to that of lab made Al-Nb-B master alloys;
- The Nb to B ratio of the master alloys has a great influence on the grain refinement of Al-Si cast alloys inoculated with Al-Nb-B master alloys. With the current lab-based manufacturing route, the best results are obtained with low B master alloys where the Nb content is higher than that of B.

Data availability

All metadata pertaining to this work can be accessed via the following link: https://10.17633/rd.brunel.9807953.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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