



Grain refining potency of Nb–B inoculation on Al–12Si–0.6Fe–0.5Mn alloy



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ABSTRACT

In a recent work we reported that the combined addition of Nb and B has higher grain refinement effectiveness than the addition of these individual chemical elements. In this work a commercial Al–12Si–0.6Fe–0.5Mn alloy is employed to fully characterise the refining potency of Nb–B inoculation. It is found that the addition of Nb powder and KBF_4 flux to Al–Si melt introduces potent nuclei with low lattice mismatch with the primary α -Al dendrites (i.e. low undercooling) and, thus, promote noteworthy grain refinement through heterogeneous nucleation. Nb–B inoculation induces a significant increment of the volumetric number of grains, decreases the undercooling needed for solidification and makes the grain size of the Nb–B inoculated material less sensitive to the cooling rate employed to solidify the material.

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1. Introduction

The grain refinement of Al and its alloys is a common practise because materials characterised by fine equiaxed α -Al structure show improved mechanical properties (strength and toughness) and better formability [1]. Grain refinement of Al and wrought Al alloy mainly relies on the addition of commercial Al–Ti–B master alloys prior casting [2–4]. The microstructure of these commercial alloys is composed of Ti-based compounds (i.e. TiB_2 and Al_3Ti intermetallics). TiB_2 particles coated with a layer of Al_3Ti constitute the heterogeneous nucleation substrates from which α -Al grains can grow whilst Al_3Ti intermetallics dissolve in the melt to form α -Al ($\text{Al}_{(l)} + \text{Al}_3\text{Ti}_{(s)} \rightarrow \alpha\text{-Al}_{(s)}$ peritectic reaction) during solidification [5–7]. The presence of free Ti in the melt is paramount for the refinement of Al because Ti has the highest growth restriction factor on Al [8]. This aspect, presence of TiB_2 , Al_3Ti and solute Ti, are responsible for the high efficiency of commercial Al–Ti–B master alloys compared to Al–Ti master alloys. Nevertheless, the performance of Al–Ti–B master alloys is quite poor in the case of cast Al alloys where Si is the main alloying element. Due to its electronic structure, Ti is characterised by very high reactivity (with both interstitial and substitutional alloying elements) and, therefore, reacts with Si to form titanium silicides which depletes the Ti content in the melt, thus reducing the efficiency of grain refinement. This phenomenon, which is especially pronounced

for alloys with Si content greater than 4 wt.% [9], is known as poisoning effect and was the subject of many investigations [3,10,11]. Different attempts to overcome this phenomenon were made although the mainstream approach consists of modification of the conventional practise and/or composition of commercial Al–Ti–B master alloys [12,13]. The first method is to have higher addition level of the Al–5Ti–1B master alloys in comparison to the industrial standard addition rate of 1–2 kg per tonne of melt. The second route implies the variation of the Ti/B ratio using near-stoichiometric (2.2 at.% Ti/1 at.% B) or sub-stoichiometric compositions. Examples are the Al–3Ti–1B and Al–1.7Ti–1.7B master alloys. The third approach is the avoidance of Ti in the master alloy such as the employment of Al–B master alloys [14–16]. All of these variants are still not very efficient and, thus, not widely used.

From the classical nucleation/solidification theory, the barrier for heterogeneous nucleation (ΔG_{net}) is related to the undercooling (ΔT) whilst the potency (P) of a heterogeneous nucleation substrate is governed by the contact angle (θ) between a spherical cap of α -Al and the substrate ($P \propto 1/\theta$) [17]. Because the values of θ are mainly unknown and difficult to assess, P is generally estimated on the base of ΔT (i.e. $P \propto 1/\Delta T$). ΔT is also strictly related to the lattice mismatch (f), which is the misfit between the lattice of the substrate and that of the nucleating phase along specific (mostly low-index) planes of the substrate, by the relationship $\Delta T \propto (f)^2$ [17]. The absolute value of ΔT is then greatly affected by both the potency of the nucleation substrates and of the cooling rate employed. Because of the influences of many different not-always-easy to determine

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aspects, and taking into account appropriate assumptions, the relationship between primary dendritic arm spacing λ_1 and growth velocity (v) can be defined as [18]:

$$\lambda_1 = \left(-\frac{72\pi^2 \Gamma_{sl} D_l \Delta T_0}{k_0} \right)^{1/4} (v)^{-1/4} (G)^{-1/2} \quad (1)$$

where Γ_{sl} is the Gibbs–Thomson coefficient, D_l is the diffusivity of the liquid phase, ΔT_0 is the equilibrium freezing range, k_0 is the partition coefficient and G is the temperature gradient (i.e. $v \cdot G = dT/dt$). Nonetheless, in practical castings, the general trend of the variation of the grain size with the cooling rate and the assessment of the influence of inoculation can be simplified to:

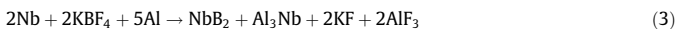
$$d = d_0 \cdot (dT/dt)^{-n} \quad (2)$$

where d_0 and n are, respectively, an alloy-dependent parameter and a parameter close to 0.5 for Al alloys [19].

Taking into account the interrelationships just presented the authors focused on the development of an alternative grain refiner whose potential heterogeneous nucleation substrates had to be characterised by three key aspects [20,21]: (i) high melting point so they do not dissolve in the melt, (ii) low lattice mismatch to significantly promote heterogeneous nucleation and (iii) high chemical stability not to react with the alloying elements (especially Si). Through an extensive searching in chemical databases looking for elements characterised by a peritectic reaction with Al and compounds with isomorphous structure to those of the Ti-based compounds of commercial Al–Ti–B master alloys, it was found that Nb is the most promising candidate. Nb can also form Nb silicides [22] but they are high temperature intermetallics and, thus, their kinetic of formation is very slow at temperature normally employed for Al casting. Consequently, they are not expected to poison the Nb–B inoculation. The aim of this work is to assess the grain refining potency of Nb–B inoculation, quantify its grain refinement effects on the Al–12Si–0.6Fe–0.5Mn alloy solidified under a great range of cooling rates as well as study the refining via heterogeneous nucleation by means of thermal analysis.

2. Experimental procedure

When Nb powder (Nb > 99.8 wt.%, particle size lower than 45 μm) and potassium tetrafluoroborate (KBF_4) are added to an Al alloy, Nb-based compounds are expected to be formed as per Eq. (3):



It is worth mentioning that the lattice mismatch between Al and Al_3Nb is quite small ($f = 4.2\%$) as in the case of Al_3Ti intermetallics [20]. The refining potency and effectiveness of Nb–B inoculation was tested on Al–12Si–0.6Fe–0.5Mn (commercially LM6 alloy). Al–12Si–0.6Fe–0.5Mn alloy without (reference) and with the addition of Nb–B powders (0.1 wt.%, targeted addition) were cast. Precisely, the Al alloy was melted at 850 $^\circ\text{C}$ during 1 h for homogenisation, the Nb powder and KBF_4 flux were added and left to dissolve and react for 2 h with intermediate manual stirring every 15 min. It is worth mentioning that the actual total amount of Nb and B present is thought to be lower due to the oxidation of the Nb powder during its addition, the poor B recovery from KBF_4 flux and the not-optimised mixing procedure. Different moulds were used to solidify the melt with and without Nb–B inoculant additions over a great range of cooling rates (0.3–100 $^\circ\text{C/s}$). Moreover, cooling curves were measured by monitoring the temperature of the melt, as a function of time, inside a glass-wool lined clay-bonded graphite crucible. The temperature was measured by means of K-type thermocouples and recorded with a NI-VI Logger collecting 100 data s^{-1} . The classical metallographic route was used to prepare the samples for microstructural analysis. In the case of the determination of the grain size, the polished samples were immersed in a HBF_4 solution and anodised. Image analysis to measure the grain size (as per ASTM-E112, intercept method) of the cast specimens was carried by means of an Axioscope A1 optical microscope.

3. Results and discussion

Fig. 1 shows the grain size as a function of cooling rate for samples produced with and without Nb–B inoculants. In the case of the

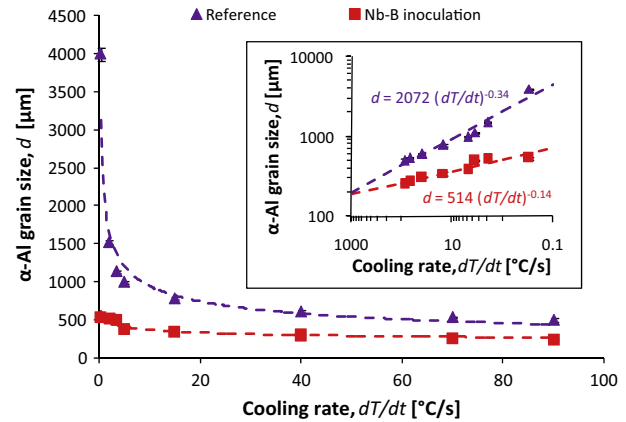


Fig. 1. Variation of the grain size with cooling rate for the Al–12Si alloy without and with Nb–B inoculation (i.e. dashed lines are fitting curves from Eq. (2)).

reference material the grain size follows the classical asymptotic behaviour (i.e. moving from coarse grains at very slow cooling rates to fine microstructure at high cooling rates). This is because the solidification of the alloy is completely governed by the heat extraction rate from the solidification front.

From Fig. 1, after Nb–B inoculation it can be noticed that the final grain size is much lower with respect to the reference materials and the variation as a function of the cooling rate is much more flattened. The switch of the trend from asymptotic to almost linear is due to the introduction of potent heterogeneous nucleation substrates (i.e. Nb-based compounds) which decrease the nucleation energy and favour the growth of a significant greater number of primary α -Al grains. Experimental data of the reference material is well described by Eq. (2) with constant $n = 0.34$. When Nb–B inoculation is used, the exponential factor n is reduced to 0.14 due to enhanced heterogeneous nucleation density. When combining the two equations it is found that: $dT/dt \propto 1/(Q)^{-n}$. The efficiency of the Nb–B inoculation is shown by the reduced slope of the curves shown in the inset of Fig. 1 which is supported by the much finer primary α -Al dendritic grains found after Nb–B inoculation of the Al–12Si–0.6Fe–0.5Mn alloy (Fig. 2). After a given cooling rate, the grain size of Al alloys can be resumed as $d = a + b/Q$, where a and b are constants related to the number of active nucleation substrates and the potency of the substrates whereas Q is the growth restriction factor [8]. The Q for Al–12Si–0.6Fe–0.5Mn alloy is 72.60 and from the work of Spittle [23] the expected grain size should be somewhat bigger than 1000 μm , which is comparable to the value of the TP-1 test reference Al–12Si–0.6Fe–0.5Mn samples (~ 3.5 $^\circ\text{C/s}$) plotted in Fig. 1 (i.e. 1140 μm). The Q for Al–12Si–0.6Fe–0.5Mn alloy with Nb addition considered in this study is 73.22 where the expected value is actually bigger because for Al alloys with Si > 3 wt.% the grain size increases with the Q value instead of decreasing. Moreover, the small increment in Q (i.e. 0.62) due to the addition of Nb has a minimal effect on the grain size. Therefore, the significant grain refinement obtained by Nb–B inoculation, whose example is shown by means of the anodised micrographs reported in Fig. 2, is due to the presence of potent nucleation sites rather than to growth restriction. In particular, Nb–B inoculation is expected to introduce potent heterogeneous nucleation substrates which are niobium aluminides (Al_3Nb) and niobium diborides (NbB_2) intermetallics as per Eq. (3). Al_3Nb and NbB_2 have isomorphous structure to Al_3Ti and TiB_2 and very similar lattice parameters, which in the case of the aluminides are exactly the same. Because of the similarities with the Al–Ti–B ternary system, the heterogeneous nucleation of α -Al grains from niobium borides and aluminides can be supposed to take place along similar planes and directions [24,25]:

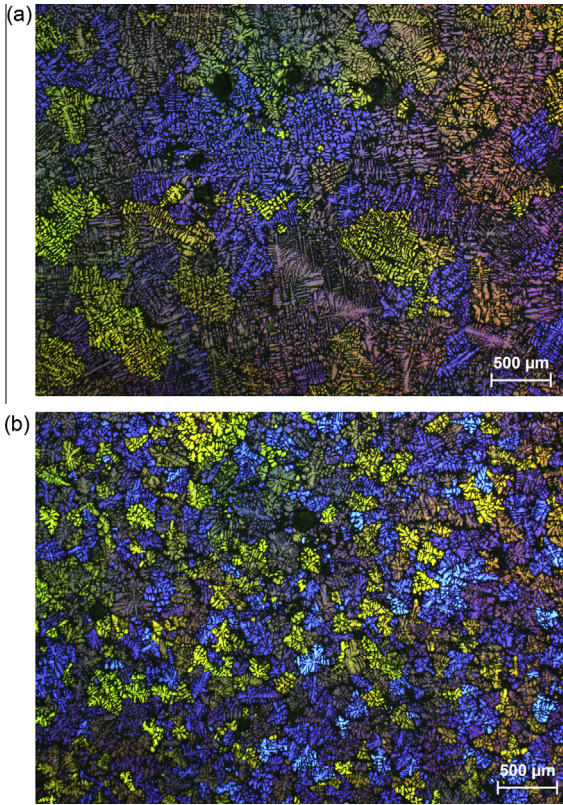
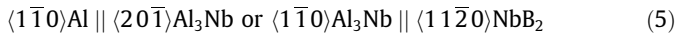
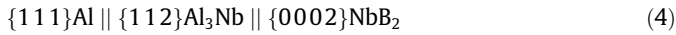


Fig. 2. Primary α -Al dendritic grain structure of the Al-12Si alloy without (a) and with (b) Nb-B inoculation (cooling rate ~ 2 °C/s).



From Fig. 2, it can be clearly seen that the grain size after Nb-B inoculation is reduced from 1500 μm to 520 μm . Correspondingly the number of grains/unit volume should be much larger and this was actually confirmed when plotting the number of grains per unit volume (N_v) versus dT/dt (Fig. 3) where the refiner efficiency is illustrated (i.e. comparison between the grains of the reference and of the Nb-B inoculated alloy).

An even clearer idea of the effect of the presence of Nb-based compounds to the Al-12Si-0.6Fe-0.5Mn alloy is given by relative difference between the number of grains prior and after inoculation (ΔN_v). It can be noticed that the $\Delta N_v/N_{v(ref)}$ curve shows an asymptotic trend which indicates that: for extremely low cooling

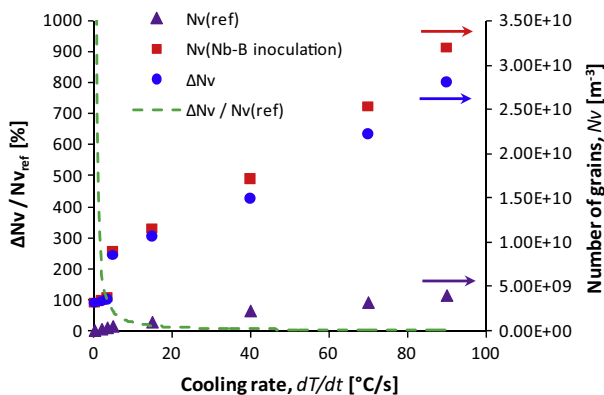


Fig. 3. Variation of the number of grains with cooling rate for the Al-12Si alloy without and with Nb-B inoculation.

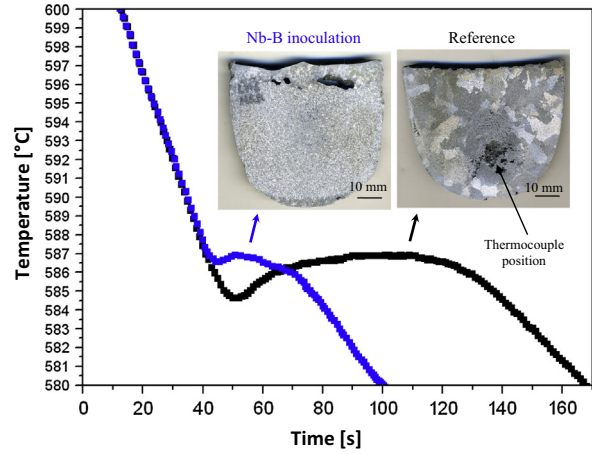


Fig. 4. Results of the thermal analysis of the Al-12Si without and with Nb-B inoculation (adapted from [19,25]).

rate single grain materials could be obtained and for extremely fast cooling rates the effect of inoculation is overcome by that of the fast heat extraction, making the employment of grain refiners redundant (i.e. unnecessary). In particular, from the inset to Fig. 1, it can be extrapolated that the reference and Nb-B inoculated alloys will be characterised by the same grain size for cooling rates in the order of 1000 °C/s. Similar grain size for materials with and without inoculation solidified at that high cooling rate (i.e. components obtained by means of the high-pressure die casting process where the cooling rate is in the range of thousands of °C/s) can be found in the literature [26]. From the work of Turnbull and Vonnegut [17] it is known that the undercooling ΔT is strongly dependent on the lattice mismatch ($\Delta T \propto (f)^2$). Consequently, the employment of potent heterogeneous nucleation substrates is expected to favour the nucleation process by lowering the undercooling needed. To further prove the potency of the Nb-based compounds added to the Al-12Si-0.6Fe-0.5Mn, thermal analysis was carried out during solidification of the alloy without and with Nb-B inoculation and the results are shown in Fig. 4 [27].

The analysis of the cooling curves (thermal analysis results shown in Fig. 4) confirms the expected decrement of the undercooling needed to solidify the Al-12Si-0.6Fe-0.5Mn alloy after the addition of potent heterogeneous Nb-based nucleation substrates. Specifically, the undercooling of the Al-12Si-0.6Fe-0.5Mn alloy is 2.5 °C whereas that of the inoculated material is 0.7 °C. The grain sizes for the corresponding samples are ~ 4000 μm and 535 μm , respectively, shown by means of the macroetched surfaces of the ingots visible as inset in Fig. 4.

4. Conclusions

It can be concluded that the addition of Nb-B (i.e. Nb-B inoculation) to Al-Si alloys introduces potent heterogeneous nucleation substrates (Al_3Nb and NbB_2) which lower the undercooling needed for the solidification process (i.e. due to the low lattice mismatch). Therefore, significant grain refinement over a wide range of cooling rates and substantial increment of the number of grains is obtained via enhanced heterogeneous nucleation making the grain size of the material less sensitive to the cooling rate.

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