



On the effect of Nb-based compounds on the microstructure of Al–12Si alloy



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HIGHLIGHTS

- The influence of Nb+B inoculation on Al–12Si is assessed.
- The grain size decreases along with the amount of Nb+B compounds.
- Nb+B inoculation makes the grain size less sensitive to the cooling rate.
- Grain refinement is obtained via heterogeneous nucleation.

ARTICLE INFO

Article history:

Received 20 October 2014

Received in revised form

24 April 2015

Accepted 29 May 2015

Available online 6 June 2015

Keywords:

Metals

Alloys

Intermetallic compounds

Optical metallography

Microstructure

ABSTRACT

Cast Al alloys are important structural materials for the lightweighting of cars and, consequently, reduction of greenhouse gases emission and pollution. The microstructure and properties of cast Al alloys could be further improved by means of grain refinement, practise which cannot efficiently be performed with common Al–Ti–B grain refiners used for wrought Al alloys. In this work we proposed the employment of Nb+B inoculation as an alternative for the refinement of the primary α -Al dendrites of cast Al–Si alloy by studying the grain refinement induced by the Nb+B inoculants as a function of key aspects such as cooling rate, fading behaviour and simulated recyclability tests. It is found that the grain size of the Nb+B inoculated material is noticeably less sensitive to the cooling rate. Nb+B inoculants are still present and promote the refinement of the Al–12Si alloy even after few hours of contact time, although some fading is detected. Furthermore, Nb+B inoculants are also still effective for enhancing heterogeneous nucleation after three remelting of the inoculated alloy. The fading behaviour and ability to retain grain refining potency after remelting are highly relevant to industrial scale applications.

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1. Introduction

The improvement of the behaviour (i.e. mechanical properties and processability) of wrought Al alloys is commonly achieved by the employment of grain refiners [1]. Specifically, commercial Al–Ti–B master alloys are added to the melt to induce the heterogeneous nucleation of a greater number of primary α -Al grains [2–4]. Current understanding is that TiB₂ particles constitute the heterogeneous nucleation substrates from which the α -Al grains grow whilst Al₃Ti dissolve inside the melt [5–7] significantly contributing to the growth restriction of the nucleated grains [8]. On the case of cast Al alloys, where Si > 4 wt.%, the addition of commercial Al–Ti–B master alloys is not effective because Ti reacts

with Si to form Ti silicides (poisoning [3,9,10]). Up to date, to the best knowledge of the authors, there are not alternative rather than the Ti-based grain refiners. In an attempt to find a reliable grain refiner for Al–Si cast alloys, which constitute the 80% of the cast Al worldwide and are employed to produce critical structural components such as engine blocks and pistons, we found that Nb is a very promising alternative because of three key aspects [11,12]. (1) Nb can form Nb-based intermetallics (i.e. NbB₂ and Al₃Nb) with isomorphous structures and similar lattice parameters to those of the Ti-based intermetallics. Therefore, a good lattice match with the α -Al phase is expected which is paramount to enhance its nucleation. (2) Nb has lower growth restriction factor than Ti (Table 1) and, consequently, its grain-refining effectiveness should be lower. (3) Nb can also form Nb silicides but they are stable at much higher temperature [13,14]. Therefore, they are not supposed to influence the grain refinement because their kinetic of formation

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at temperature used for Al casting is very slow. The most adopted theory to address the potency of grain refinement via heterogeneous nucleation and the relative variation of the grain size (d) is:

$$d = a + \frac{b}{Q} \quad (1)$$

where a is an experimental parameter related to the number density of active nucleant particles, b is an experimental parameter correlated to the intrinsic potency of the nucleants and Q is the growth restriction factor [8]. The factor Q depends on the inherent constrain that each alloying element induces on the growth of α -Al grains during the solidification of Al alloys where their effects are, normally, summed up:

$$Q = m_1 C_{0,1} (k_1 - 1) + m_2 C_{0,2} (k_2 - 1) + \dots + m_{i-th} C_{0,i-th} (k_{i-th} - 1) \quad (2)$$

In Eq. (2), m_i corresponds to the gradient of the liquidus line of every alloying element in binary phase diagrams, $C_{0,i}$ is the percentage of the alloying element and k_i is its partition coefficient. The data needed to calculate the Q value for some alloying elements and some of the elements employed in commercial grain refiners (e.g. Ti and Zr) are shown in Table 1.

The foundation of Eq. (1) is that heterogeneous nucleation progresses simultaneously with the constitutional undercooling (ΔT_n) both of which are related to the variation in grain size ($d \propto \Delta T_n / Q$) under the assumption that in binary phase diagram Q is essentially ΔT_n for a specific kC_0 solute content.

The effect of the cooling rate on the variation of the grain size of an alloy was assessed through Eq. (3):

$$d = d_0 \cdot (dT/dt)^{-n} \quad (3)$$

where d_0 and n are alloy-dependent parameters.

The aim of this study is to report and discuss the grain refining effectiveness of Nb+B inoculation on a commercial Al–12Si alloy by considering different level of addition in order to find the best addition rate. The refining potency and effects of Nb+B inoculation are assessed by an in-depth study of different key aspects, such as influence of the cooling rate on the grain size, fading behaviour and simulated recyclability tests by remelting of the inoculated material.

2. Experimental procedure

The materials purchased to carry out the study about the grain refining potency of Nb+B inoculation were: Nb powder (Nb > 99.8 wt. %, <45 μ m), potassium tetrafluoroborate (KBF_4) and the commercial Al–12Si–0.6Fe–0.5Mn alloy (i.e. equivalent to LM6 or A431 alloy). It is worth mentioning that this alloy has relatively high Fe content to increase its fluidity because it is normally

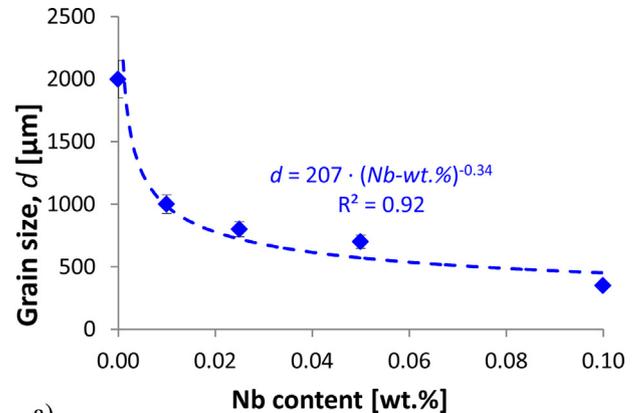
Table 1

Data needed to calculate the Q value of some chemical elements relevant for Al alloys [8].

Parameter	Chemical element					
	Ti	Zr	Nb	Si	Fe	Mn
m_i	33.3	4.5	13.3	−0.66	−3.0	−1.6
k_i	7.8	2.5	1.5	0.11	0.22	0.94
Max $C_{0,i}$	0.15	0.11	~0.15	~12.6	~1.8	1.9
Reaction type	^a PE.	^a PE.	^a PE.	^b EU.	^b EU.	^b EU.
$m_i(k_i-1)$	~220	6.8	6.6	5.9	2.9	0.1

^a PE: peritectic reaction.

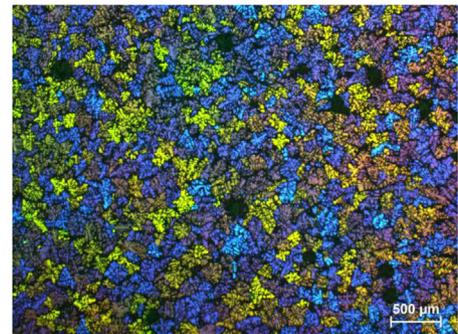
^b EU: eutectic reaction.



a)



b)

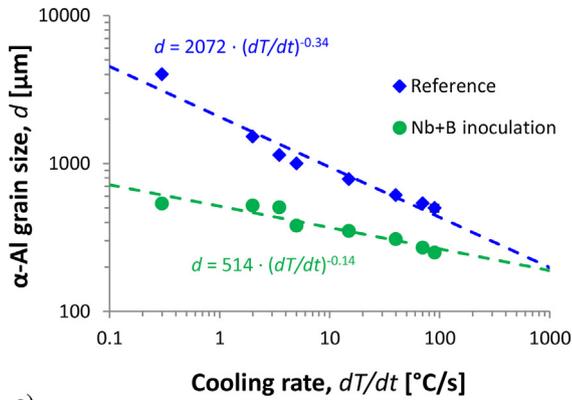


c)

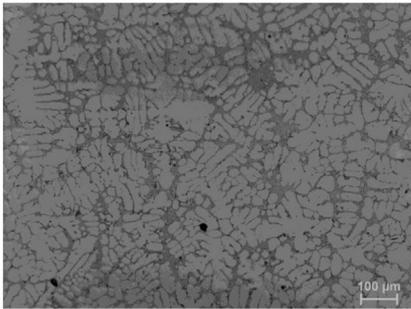
Fig. 1. Effect of Nb+B inoculation on Al–12Si alloy cast at 740 °C (cooling rate ~ 0.5 °C/s): a) variation of the grain size as a function of Nb, b) polarised light micrograph of the reference alloy and c) polarised light micrograph of the Nb+B inoculated alloy.

processed by high pressure die casting. This alloy also contemplates Mn in its chemical composition because Mn permits to modify the needle-like morphology of the Fe-based intermetallics that form upon solidification [15].

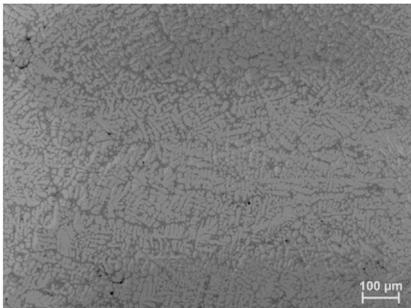
Nb+B inoculation experiments were performed adding directly the targeted percentage of Nb powder and KBF_4 flux to the melt [16]. Specifically, the ratio between Nb and B was kept constant (i.e. 1:1) and different “targeted” addition rates were used: (0 wt.% (i.e. reference), 0.01 wt.%, 0.025 wt.%, 0.05 wt.% and 0.1 wt.%). The alloy was melted inside a clay bonded graphite crucible in an electric furnace at 850 °C during, at least, 1 h prior to proceed with the addition of the Nb powder and KBF_4 flux. The melt was left to interact with the chemical elements during 2 h with intermediate stirring every approximately 15 min. It is worth mentioning that although specific percentages of Nb and B were targeted, the actual amount of these elements is expected to be slightly lower because some of the Nb powder oxidised during addition and complete recovery of B from KBF_4 flux at lab scale is difficult [17]. Nb-based intermetallics, which will act as heterogeneous nucleation



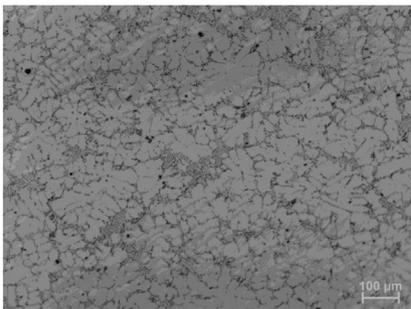
a)



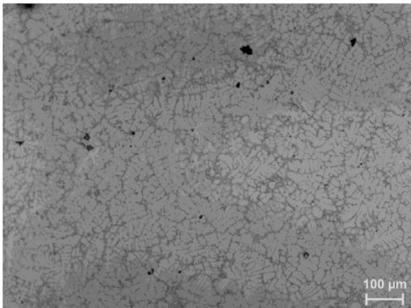
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c)

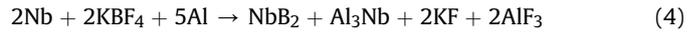


d)



e)

substrates, are expected to form as per Eq. (4):



Reference samples as well as specimens with different Nb+B addition rates (i.e. 0.01–0.1 wt.%) were considered in order to promote the heterogeneous nucleation of the Al–12Si and fully characterised the potential of Nb+B inoculation. On the base of this initial part of the study, the addition level was then set to 0.1 wt.% (i.e. targeted addition). Subsequently, the study of the effect of the cooling rate (0.3–100 °C/s) was performed using various moulds to solidify the materials. The classical metallographic route of SiC papers grinding plus OPS polishing was used to prepare the samples for their microstructural analysis, which was performed with an Axioscope A1 optical microscope. Polarised light micrographs taken at the optical microscope were used for the measurement of the grain size as per ASTM E112-13 (i.e. linear intercept method).

3. Results and discussion

Fig. 1 shows the variation of the grain size of the Al–12Si alloy cast at 740 °C (cooling rate ~ 0.5 °C/s) versus Nb content. The grain size decreases asymptotically with the increment of the targeted amount of Nb added to the molten metal due to the higher content of potential heterogeneous substrates (i.e. Nb-based compounds) available for the nucleation of the primary α -Al dendrites.

The significant grain size difference for the Al–12Si alloy without and with Nb+B inoculation can be seen by comparing the representative polarised light micrographs shown in Fig. 1b) and c). Consequently, it is confirmed that the grain size reduction is actually taking place via the heterogeneous nucleation mechanism as a consequence of the combined addition of Nb and B and, therefore, the formation/presence of Nb-based compounds.

The variation of the grain size versus the cooling rate is presented in Fig. 2 where it can be seen that the grain size decreases with the increment of the cooling rate (i.e. moving from coarse grains at very slow cooling rates to fine microstructure at high cooling rates) independently of the employment of inoculants. This is because the higher the cooling rate, the faster the heat extraction from the solidification front and the lower the time for grain growth.

From Fig. 2, it can be seen that Nb+B inoculation leads to the decrement of both d_0 and n parameters. Specifically, the experimental data of the reference material are well described by Eq. (3) with an exponential factor $n = 0.34$, which is reduced to 0.14 after Nb+B due to enhanced heterogeneous nucleation density. By combining Equations (1) and (3), it is found that: $dT/dt \propto 1/(Q)^{-n}$. Therefore, the effectiveness of the Nb+B inoculation is clearly indicated by the reduction of the slope of the fitting curves in agreement with the much finer primary α -Al dendrites obtained in the Nb+B inoculated Al–12Si alloy (Fig. 1b and c). Eq. (1) (i.e. $d = a + b/Q$) is also useful to compare the data for specific cooling rates, where the Q value for the reference material is 72.60 whilst that for the alloy inoculated with 0.1 wt.% of addition IS 73.22. Commonly, as reported from Spittle [18], in the case of Al alloys with Si content greater than 4 wt.% (i.e. Al cast alloy) the grain size

Fig. 2. Effect of Nb+B inoculation on Al–12Si alloy as a function of the cooling rate: a) variation of the grain size with cooling rate for the Al–12Si alloy without (diamonds) and with Nb+B inoculation (circles), i.e. dashed lines are fitting curves from Eq. (3), b) micrograph of the slow cooled (-2 °C/s) reference alloy, c) micrograph of the fast cooled (-100 °C/s) reference alloy, d) micrograph of the slow cooled (-2 °C/s) Nb+B inoculated alloy and e) micrograph of the fast cooled (-100 °C/s) Nb+B inoculated alloy.

Table 2

Parameters used to study the sedimentation of the potential heterogeneous nucleation substrates (i.e. Nb-based compounds) inside the molten Al–12Si alloy.

Parameter	Value
Diameter of the substrates, ϕ [μm]	10–20
Gravitational acceleration, g [m/s^2]	9.81
Density of NbB_2 , ρ_{sub} [g/cm^3]	6.97
Density of Al_3Nb , ρ_{sub} [g/cm^3]	4.54
Density of AlB_2 , ρ_{sub} [g/cm^3]	3.19
Density of liquid Al, ρ_{liq} [g/cm^3]	2.37
Viscosity of liquid Al @ 680, η [mPa s]	1.3
Max sedimentation height, h [mm]	200

increases with the increment of the Q . The grain size of the TP-1 test (~ 3.5 °C/s) reference alloy (i.e. 1140 μm in Fig. 2) is consistent with the prediction of Spittle [18] (grain size > 1000 μm). Thus, the increment of Q due to Nb addition (i.e. 0.62) does not justify the important refinement attained through Nb+B inoculation as visually shown by means of the polarised light micrographs of Fig. 1. This analysis further proves that Nb+B inoculation introduces potent heterogeneous nucleation substrates, which are niobium aluminides (Al_3Nb) and niobium diborides (NbB_2) intermetallics as per Eq. (4), responsible for the refinement of the microstructure of the Al–12Si alloy. From the micrographs of Fig. 2, the actual amount of primary α -Al dendrites is influenced by the cooling conditions but not noticeable differences can be highlighted when comparing the reference alloy with the inoculated one. The presence of a relative significant amount of primary α -Al dendrites in this near-eutectic alloy is mainly due to the solidification of the material in non-equilibrium conditions. Comparable results were found in the LM25 alloy (A356) [19].

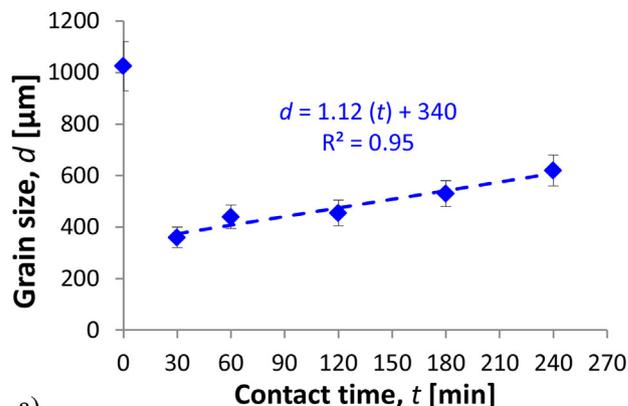
It is well known that the efficiency of grain refiners decreases with the increment of the contact time (i.e. time after the addition of the master alloy to the melt). This is due to the fact that the inoculants, such as the Ti-based compounds, are characterised by higher density and, thus, tend to sediment. This phenomenon is called “fading” and can be partially recovered by stirring the melt prior casting. The non-recoverable fading is owed to particles forming sludge at the bottom of the crucible [20] but fading can also be caused by solute poisoning of inoculants particles and agglomeration of inoculants particles into clusters [21]. The sedimentation velocity (V) of the heavy potential heterogeneous nucleation substrates (i.e. Nb-based compounds, in this work) inside the molten Al was studied by considering Stokes’ law:

$$V = \frac{\phi^2 \cdot g \cdot (\rho_{\text{sub}} - \rho_{\text{liq}})}{18 \cdot \eta} \quad (5)$$

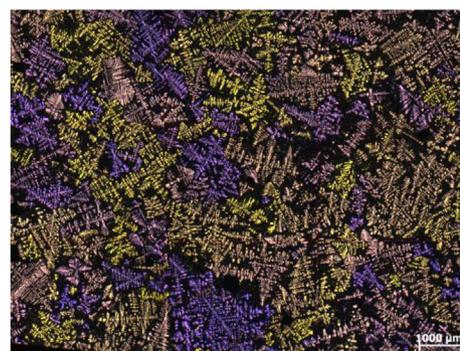
where ϕ is the diameter of the substrates, g is the gravitational acceleration, ρ_{sub} and ρ_{liq} are the density of the substrates and of molten Al, respectively, and η is the viscosity of liquid Al. The parameters used are reported in Table 2 and the following assumptions were made for the study: the substrates are spherical, they are sufficiently dispersed as not to interact among them and no strong agitation (turbulent flow) is present.

The fading behaviour of Nb+B inoculants on the Al–12Si alloy was studied and the results are shown in Fig. 3 (cast at 680 °C, cooling rate ~ 3.5 °C/s).

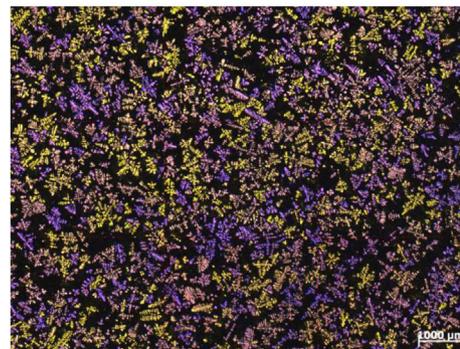
From Fig. 3, the grain size of the reference cast at 680 °C is lower (Fig. 3b) than that cast at 740 °C (Fig. 1) due to more efficient heat extraction and faster cooling rate when using a lower pouring temperature. After 30 min of contact time the grain size is reduced to 360 μm which is consistent with the results of Fig. 1 for the same



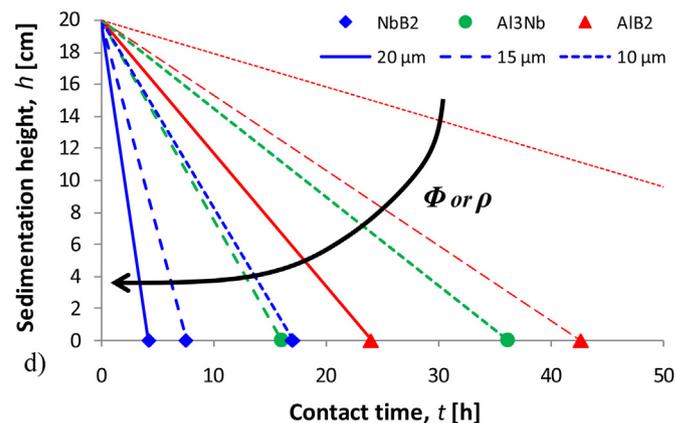
a)



b)



c)



d)

Fig. 3. Results of the fading analysis of the Nb+B inoculated Al–12Si alloy cast at 680 °C (cooling rate ~ 3.5 °C/s): a) grain size vs. contact time, b) polarised light micrograph of the reference alloy, c) polarised light micrograph of the alloy after 4 h of inoculation and d) analysis of the sedimentation of the potential heterogeneous nucleation substrates (diamonds: NbB_2 , circles: Al_3Nb and triangles: AlB_2).

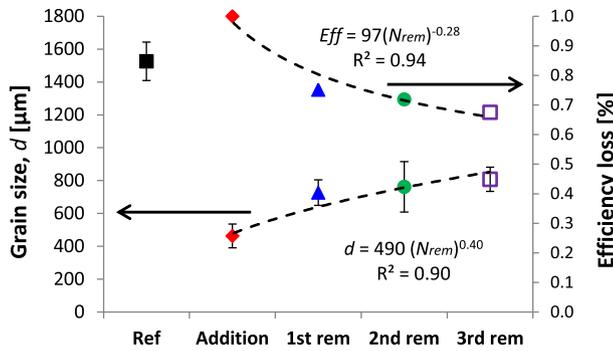


Fig. 4. Results of the recyclability by remelting test fading analysis of the Nb+B inoculated Al–12Si alloy cast at 680 °C (cooling rate ~ 2 °C/s): square: reference, diamond: addition of the inoculants, triangle: 1st remelting, circle: 2nd remelting and empty square: 3rd remelting.

Nb+B addition level (i.e. 0.1 wt.% Nb targeted addition). The achievement of the same refinement when using two importantly different pouring temperatures further confirms that Nb+B inoculation makes the final grain size of the Al–12Si alloy less sensitive to the cooling rate as found from the study of the effect of the cooling rate (Fig. 2). Due to the sedimentation of the Nb-based compounds the grain size increases continuously in the range of 470 μm after 2 h and 630 μm after 4 h (Fig. 3c). The results shown in Fig. 3 are comparable to those of other Ti-based master alloys, such as Al–5Ti–1B [22]. Fig. 3d) shows the simulated sedimentation behaviour (Eq. (5)) of three kinds of intermetallics, precisely NbB₂, Al₃Nb and AlB₂, which are thought to form when the Nb powder and KBF₄ flux are added to the molten metal. It is worth mentioning that although the AlB₁₂ could form, this compound was not considered because the time for its sedimentation is, at least, one order of magnitude slower in comparison to the other intermetallics due to the fact that its density (i.e. 2.56 g/cm³) is much more similar to that of molten alloy (Table 2). From Fig. 3d), it can be seen that there is quite an important variation of the sedimentation time depending on the type of intermetallic. Particularly, the higher the density of the compound the faster its sedimentation and, thus, the trend of the sedimentation velocity is: NbB₂ > Al₃Nb >> AlB₂. Moreover, the final sedimentation time is highly influenced by the diameter (ϕ) of the potential heterogeneous nucleation substrates where the lines shown in Fig. 3d) correspond to 20 μm (solid line), 15 μm (dash line) and 10 μm (fine dash line). The ϕ values considered were estimated from the work of Greer et al. [23]. The overall fading behaviour of the Nb+B inoculated Al–12Si alloy is a compromise between the sedimentation of these different types of intermetallics, each one having a different particle size distribution.

The total contact time needed to completely loose the effect of the Nb+B inoculation can be evaluated from the simple linear regression presented in Fig. 3a), roughly 10 h from which the corresponding diameter for the fading of each type of intermetallics can be estimated as 13.2 μm (NbB₂) 19.3 μm (Al₃Nb) and 31.4 μm (AlB₂), respectively.

Another important aspect of Al and its refinement is the recyclability of the scraps at the end of their lifetime cycle, scrap which can either be generated internally in a cast house or coming from real products such as structural components. The motivation of the recycling of Al alloys is because the energy needed and greenhouse gases emitted to obtain 1 kg of recycled Al are roughly 5% of those necessary/released to extract 1 kg of virgin material from its ores. The recyclability of the Nb+B inoculated Al–12Si alloys (0.1 wt.% targeted addition) was studied remelting the same material up to 3 times after the initial addition without any further addition of

Nb+B inoculants. The results of the remelting test of the Al–12Si cast at 740 °C are presented in Fig. 4 where the first point that can be noticed is the coarse grain size of the reference material (~ 1500 μm).

Once again, the initial addition of Nb+B inoculants reduces the grain size of the primary α -Al dendrites and the value is consistent with the previous results (Figs. 1 and 2). From the linear regression reported in Fig. 4, it can be seen that the variation of the grain size with the number of remelting can be approximated with the power law (Eq. (6)):

$$d = 490 \cdot (N_{rem})^{0.40} \quad (6)$$

On the base of this equation, the estimated number of remelting processes needed to complete lose the effect of Nb+B inoculation is 17. It is worth mentioning that in this approximation no sedimentation of the potential heterogeneous nucleation substrates was considered because, in every experiment, the alloy is melted and kept the minimum time required to reach a homogeneous temperature inside the melt prior to its casting. Moreover, the trend is affected by the experimental procedure followed: initially the sample for microstructural analysis is cast and, afterwards, the remaining of the melt is cast for further remelting. Nevertheless, the power-law equation provides a sufficiently reliable estimation of the total number of substrates which become active during the solidification of the remelted alloy. The efficiency of the Nb+B inoculation lost through the different re-processing of the alloy is also shown in Fig. 4. The efficiency loss was calculated as per Eq. (7) considering that the initial inoculation of the Al–12Si alloy leads to a decrement of the grain size of approximately 1000 μm :

$$Efficiency\ loss = 100 - \sum \frac{d_{N+1} - d_N}{d_{Ref} - d_{Add}} \quad (7)$$

where d_N is the grain size (comparable to the number of active substrates) at the n -th remelting, d_{Ref} is the grain size of the reference alloy and d_{Add} is the grain size of the alloy freshly inoculated. The loss of efficiency is thought to be due the combined effect of interrelated factors such as decreasing number of potential heterogeneous nucleation substrates available, lowering of the total undercooling induced by the presence of the inoculants, lower number and sedimentation of the particles with bigger diameter and higher density (Fig. 3). Although of all these factors, the efficiency of Nb+B inoculants is still approximately 65% of its initial potency after the 3rd remelting. Consequently, depending on the grain size acceptance level, much lower addition of further Nb+B inoculants or, even, no further addition would be required when recycling the alloy.

4. Conclusions

From this study where a commercial Al–12Si alloy was inoculated with different level of Nb+B addition to assess the grain refining potency of Nb+B inoculation it can be concluded that in-situ formed Nb-based intermetallics compounds are potent heterogeneous nucleation substrates with high potency for the refinement of Al–Si cast alloys. The primary α -Al dendritic grain size varies with the addition level of Nb and B. Moreover, significant grain refinement over a wide range of cooling rates is obtained via enhanced heterogeneous nucleation making the grain size of the material less sensitive to the cooling rate. Nb+B inoculants are characterised by some fading which is still acceptable after 4 h of contact time. Moreover, alloys refined by means of Nb+B inoculants can be recycled obtaining a fine grain structure with small addition

or no further addition of inoculants after the first initial addition. Concluding, Nb+B inoculation is a promising candidate for the refinement of cast Al alloy which could lead to their wider employment in the automotive industry with the resultant intrinsic advantages of lighter structural component from an environmental point of view.

Acknowledgements

The authors are thankful for the financial support from the Technology Strategy Board (TSB) through the TSB/101177 Project and to the Engineering and Physical Sciences Research Council (EPSRC) through the EP/J013749/1 and EP/K031422/1 Projects.

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