

Engineering the heterogeneous nuclei in Al-Si alloys for solidification control

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ARTICLE INFO

Article history:

Received 1 October 2016

Received in revised form 2 November 2016

Accepted 3 November 2016

Keywords:

Aluminium alloys

Solidification

Heterogeneous nucleation

Inoculation

Grain size

Grain refinement

ABSTRACT

Aluminium alloys are particularly advantageous for transportation industries to reduce the weight of the vehicles and thus pollution. The optimisation of the performances of Al alloys can be achieved by engineering and enhancing the heterogeneous nucleation of the melt. In this work, we demonstrate how the inoculation of commercial Al-Si alloys by Nb-based phases permits to improve and control the solidification process. We show that NbB₂/Al₃Nb are potent heterogeneous nucleation substrates for Al-Si alloys. The improved nucleation makes the material structure less dependent on the processing conditions such as solidification time and chemistry of the alloy (i.e. Si content). This permits to design and fabricate lighter structural components with improved and more isotropic performances.

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1. Introduction

Aluminium (Al) and its alloys are becoming important structural materials in many transportation industries, and especially the automotive, due to their low density. The reduction of the vehicle weight translates in lower fuel consumption and lower greenhouse gases emission [1]. Al alloys are commonly divided into wrought and cast alloys. The former are obtained using downstream hot/cold deformation methods like extrusion of billets. The latter are produced by casting processes such as die casting. Therefore, at some stage, either class of alloy undergoes solidification (i.e. nucleation plus growth).

As per the classical nucleation theory, the critical activation energy (ΔG^*) to form a stable nucleus and the critical radius (r^*) for the nucleus to grow into a crystal with long order atomic arrangement are inversely proportional to the undercooling, ΔT (i.e. the actual temperature in the solidification front). In practical instances, nucleation does occur heterogeneously on solid substrates such as mould walls. The reduction in ΔG^* is a function of the contact angle (θ) between the substrate and the liquid metal.

The experimental measurement of θ is not an easy task and only values for specific substrate/nucleating phase systems (such as for example MgO/Al) are available in the literature. However, it is known that the lower θ the higher the intrinsic *Potency* of the

substrate (*Potency* $\propto 1/\theta$) and the *Potency* can be estimated if ΔT is measured (*Potency* $\propto 1/\Delta T$).

At atomic scale, the *Potency* is dictated by the mismatch (f) between the lattices of the substrate and that of the nucleating phase. Potent substrates to promote nucleation can intentionally be added to the molten metal, an industrial practise known as inoculation. Summarising, the highest reduction in ΔG^* is obtained with the lowest ΔT which is achieved via introducing substrates with high *Potency*. Nonetheless, the substrates have also to be chemically stable to be effective [2].

Inoculation of Al alloys is a common industrial practise in the last half century as this leads to the refinement of the grain structure enhancing the deformability in downstream processes [3–5]. Inoculation is generally carried out by means of Al-Ti-B master alloys, containing Ti-based substrates (i.e. TiB₂ and Al₃Ti), that are added to the melt prior to casting [6].

The high efficiency of commercial Al-Ti-B master alloys relies on both the low f between the Ti-based substrates and α -Al as well as the high growth restriction factor (Q) of Ti on Al [7]. For cast Al alloys, the ones based on the Al-Si diagram, the effect of inoculation by Ti-based substrates is significantly limited due to their poor chemical stability. This is because these substrates lose their *Potency* due to the phenomenon known as poisoning. That is, Ti has high affinity with Si and therefore a layer of Ti silicide is formed on the outer surface of the Ti-based substrates. Ti silicides have greater f and the melt is depleted of Ti [8]; both aspects reduce the *Potency* of Ti-based substrates. The most widely used Al-Ti-B master alloys (such as Al-5Ti-1B or Al-3Ti-1B) have Ti/B atomic ratio >2.2 where the excess of Ti favours poisoning. Alternative Ti-containing

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master alloys with stoichiometric ($Ti/B = 2.2$) or sub-stoichiometric ($Ti/B < 2.2$) compositions or where B is replaced by C were proposed and investigated for Al-Si alloys; however, their performances are still quite poor [9,10].

We recently reported the discovery that inoculation of Al-Si cast alloys with Nb + B is very effective [11,12]. Nb-based substrates (i.e. NbB_2 and Al_3Nb) are isomorphous with Ti-based substrates and therefore ideal in term of *Potency* to nucleate α -Al.

Nevertheless, Nb-based substrates are not subjected to poisoning in Al-Si cast alloys. At temperatures used in Al foundries (700–800 °C), Nb-based substrates have superior chemical stability with respect to Ti-based substrates [13].

In our original study, Nb + B inoculation of Al-Si alloys was performed and proven by directly adding Nb and KBF_4 powders to the molten alloy [11,12]. This processing route is not optimum at industrial level, because of the poor yield of Nb and B recovery and the corrosive nature of KBF_4 .

We further developed an alternative inoculation route considering the approach of creating Al-Nb-B master alloys and tested it on various commercial Al-Si solidified in a broad window of solidification conditions. The aim of this work is to demonstrate that the enhancement of the nucleation process through chemically engineered heterogeneous substrates permits one to produce materials whose cast structure is less dependent on both their intrinsic chemical composition (i.e. Si content) and processing conditions like solidification time. In particular, the effects that an Al-Nb-B master alloy containing Nb-based substrates have on the solidification (nucleation/growth) of Al-Si alloys are presented and elucidated.

2. Materials and methods

2.1. Production/characterisation of the heterogeneous nuclei

We targeted a nominal composition of 2 wt.% of Nb and 2 wt.% of B to take into account the poor yield of recovery previously found [11,12]. The Al-Nb-B master alloy was produced by melting pure Al, Nb powder and an Al-5B master alloy in a clay bonded graphite crucible at 850 °C for 3 h with intermediate manual stirring. Prior to its casting, the Al-Nb-B master alloy was cooled down to approximately 700 °C.

Microstructural analysis was done on polished and deep-etched samples using a Zeiss Supra 35VP FEG microscope. EDS was performed to obtain semi-quantitative chemical composition data. 3 mm discs were cut from slices of the Al-Nb-B master alloy and ground with SiC papers to a thickness of approximately 60 μm . A Gatan ion polishing equipment (5 kV, incident angle of 6°) was used for the final thinning of the samples. A JEOL 2200F-TEM operated at 200 keV was employed to study the features of the Nb-based substrates.

2.2. Effects of heterogeneous nuclei on nucleation phenomena

A series of commercial Al-Si cast alloys were inoculated with the Al-Nb-B master alloy and their chemical compositions are: Al-7Si-0.4Mg-0.2Fe, Al-8.5Si-0.3Mg-0.1Fe, and Al-10.5Si-4Cu-1.4Zn-0.2Mg-1.0Fe. The targeted addition rate was 0.1 wt.% Nb even if it is expected that the actual final contents of Nb and B are lower. The Al-Si alloys were melted at 790 °C for 1 h and then cast from 740 ± 3 °C. In the case of inoculation, the contact time was 30 min.

Slow cooling rate (~ 0.3 °C/s) curves were recorded using type-K thermocouples. In this thermal analysis, the difference between the minimum and the recalcence temperature of the undercooling peak is the driving force for nucleation ($\Delta T = T_g - T_{min}$) and is related to the intrinsic *Potency* of the heterogeneous nuclei.

A broad window of cooling conditions was investigated for Al-Si alloys using different permanent steel and copper moulds pre-heated at 250 °C. Microstructural analysis and grain size measurements (as per ASTM E112, intercept method) were performed on the Zeiss Axioscope A1 optical microscope. For the latter quantification, polarised light micrographs of samples anodised using a HBF_4 solution and a current of 10V/1 A were used.

3. Results

3.1. Characterisation of the heterogeneous nuclei

SEM analysis of the Al-Nb-B master alloy revealed a relatively uniform distribution and dispersion of agglomeration of heterogeneous substrates (0.5–15 μm) embedded into the Al matrix. EDS chemical analysis of deep-etched Al-Nb-B master alloy and XRD analysis confirmed the formation of Nb-based substrates that remain stable after casting of the master alloys (Fig. 1). The Nb-based heterogeneous nuclei have the following crystal lattice: tetragonal for Al_3Nb (DO_{22}) [14,15] and hexagonal for NbB_2 ($P_{6/mmm}$) [16].

The NbB_2 substrates present a typical hexagonal plate-like morphology as per the TEM bright field image shown in Fig. 2a. The $\{0001\}$ basal plane of the NbB_2 substrates is visible. Heterogeneous nucleation of α -Al is believed to happen on the $\{0001\}$ surface of borides [17].

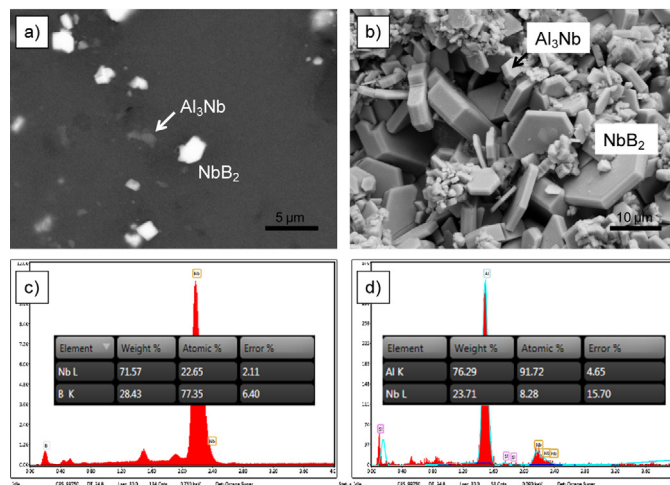


Fig. 1. Representative SEM results of the heterogeneous nuclei present in the Al-Nb-B master alloy: (a) SE micrograph showing the distribution of the Nb-based substrates in the Al matrix, (b) SE micrograph showing the size/morphology of the NbB_2/Al_3Nb substrates, and (c, d) semi-quantitative chemical EDS analysis of the NbB_2/Al_3Nb substrates, respectively.

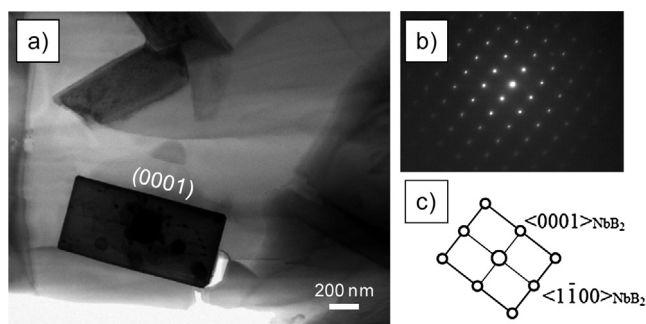


Fig. 2. Representative TEM results of the heterogeneous nuclei present in the Al-Nb-B master alloy: (a) bright field micrograph showing the hexagonal plate-like morphology of NbB_2 substrates, and (b, c) diffraction pattern of the NbB_2 substrates.

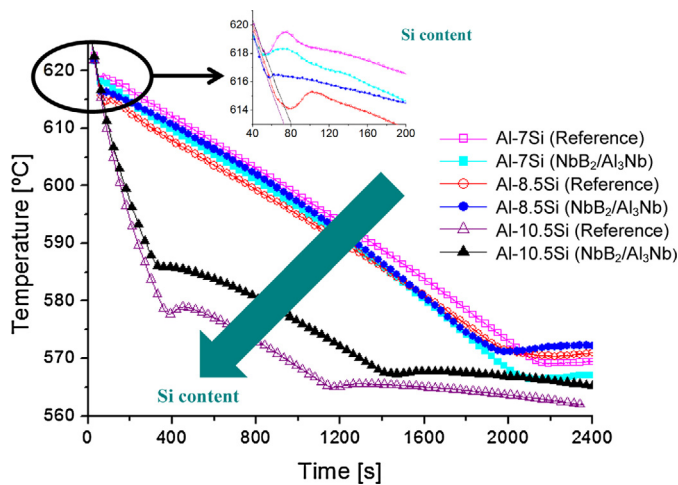


Fig. 3. Thermal analysis ($\sim 0.3^\circ\text{C/s}$) of the Al-Si alloys without (reference) and with inoculation ($\text{NbB}_2/\text{Al}_3\text{Nb}$) showing the influence of the Si content and addition of engineered heterogeneous nuclei on the solidification phenomena (i.e. nucleation of the primary α -Al grains and nucleation of the secondary eutectic Si phase).

Table 1

Undercooling data of nucleation of the primary α -Al grains (ΔT_α) and of the nucleation of the secondary eutectic Si phase (ΔT_{eu}) obtained from thermal analysis curves shown in Fig. 3.

Material		Si content [wt.%]		
		7.0	8.5	10.5
Reference	ΔT_α	1.7	1.4	1.4
	ΔT_{eu}	1.4	1.8	0.9
$\text{NbB}_2/\text{Al}_3\text{Nb}$ inoculation	ΔT_α	0.6	0.3	0.4
	ΔT_{eu}	1.1	1.3	0.7

3.2. Effects of heterogeneous nuclei on nucleation phenomena

From thermal analysis results (Fig. 3 and Table 1), the inoculation of the commercial Al-Si alloys by means of $\text{NbB}_2/\text{Al}_3\text{Nb}$ substrates reduces the ΔT needed for the nucleation of both

primary α -Al grains and the secondary eutectic Si phase (i.e. lower ΔC^*) [18].

The cooling curves are shifted towards lower solidification temperature with the Si content as per the binary Al-Si phase diagram. It is worth mentioning that the alloys show a quite pronounced eutectic nucleation recalescence (ΔT_{eu}) due to the fact that being commercial alloys they contain strontium (Sr). This element is normally used to “modify” the morphology of the eutectic phase from faceted plate-like crystals to a fine fibrous structure [19].

The size of the grains formed on the reference Al-Si alloys increases with the Si content (Fig. 4); this is expected for Si contents above ~ 3 –4 wt.% Si [20]. The grain size does also increase with Q . Although this is known for Al-Si alloys with Si > 3 –4 wt.%, a higher Q should lead to a finer grain structure. After inoculation the grain size is constant with both the increment of the Si content and Q .

The reference Al-Si alloys are also characterised by columnar grains visible in the outer diameter of the macroetched cross sections (examples as inset in Fig. 4). This indicates that directional solidification happened from the walls of the mould. Consequently, a columnar to equiaxed transition (CET) zone is also present. The formation of columnar grains, hence of the CET, can successfully be prevented via inoculation with $\text{NbB}_2/\text{Al}_3\text{Nb}$ substrates (Fig. 4).

The size of the primary α -Al dendrites increases with the solidification time because of the slower heat extraction from the solidification front. Thus a higher ΔT and a larger r^* are needed and there is more time for grain growth. All these factors contribute to the coarsening of the dendrites (Fig. 5). The inoculation with $\text{NbB}_2/\text{Al}_3\text{Nb}$ substrates significantly reduces the grain size independently of the Si content or the solidification time. However, the effect of inoculation becomes more important with the solidification time.

4. Discussion

As per SEM/TEM analysis, the processing parameters used are adequate to form stable Nb-based substrates ($\text{NbB}_2/\text{Al}_3\text{Nb}$) in situ.

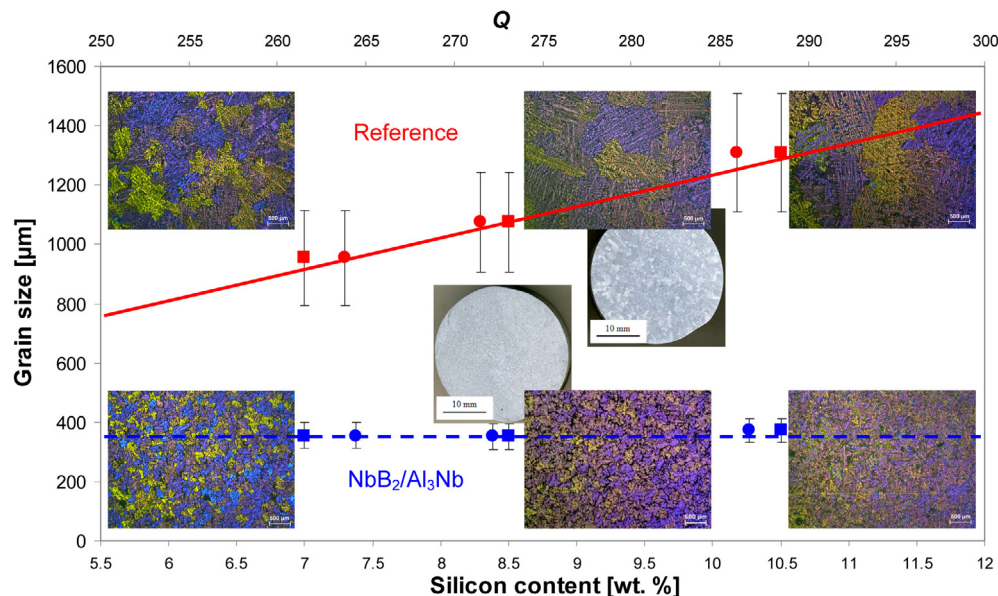


Fig. 4. Variation of the grain size versus silicon content (squares) and growth restriction factor Q (circles) of Al-Si alloys without (reference) and with inoculation ($\text{NbB}_2/\text{Al}_3\text{Nb}$). Representative polarised light micrographs as well as macroetched cross sections are also shown.

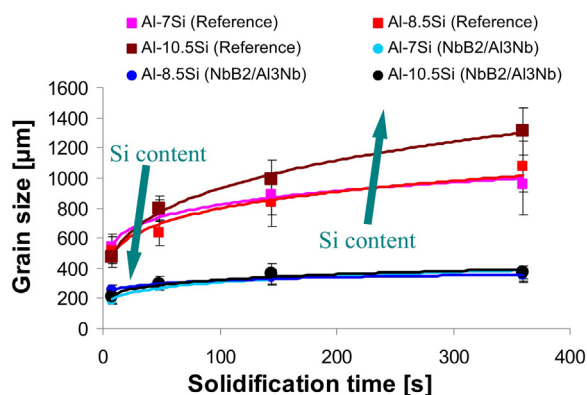
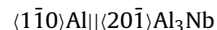
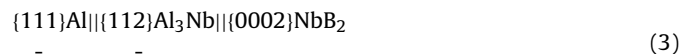


Fig. 5. Variation of grain size versus solidification time of Al-Si alloys without (reference) and with inoculation (NbB₂/Al₃Nb). For reference alloys the grain size is significantly affected by the solidification time and Si content. After inoculation the grain size is far less dependent on the solidification conditions and there is not a clear dependence from the Si content.

These are formed as per Eqs. (1) and (2) because pure Nb was added to the molten Al in which the Al-5B master alloy was dissolved:



The formation of Nb borides at the expenses of the dissolution of Al borides from the Al-5B master alloy is due to the higher thermodynamic stability of the former as their enthalpy are -251 kJ/mol^{-1} and -151 kJ/mol^{-1} for NbB₂ and AlB₂, respectively [21]. The Nb-based substrates are rather homogeneously distributed in the Al matrix and they come as agglomeration of Nb borides and aluminides. These agglomerations are composed of various polygonal and plate-like crystals grown along not specific direction and with no particular orientation relationship (Fig. 1b). TEM results (Fig. 2) combined with crystallography data as well as the current scientific understanding of the inoculation of Al [17] indicate that the heterogeneous nucleation of α -Al dendrites is more likely to happen on specific planes and directions. The orientation relationships are as follow:



or



The reduction of the undercooling induced by the presence of engineered heterogeneous nuclei is an indirect measurement of the *Potency* [22]. This is because the lower ΔT the lower f (i.e. $\Delta T \propto f^2$) as demonstrated by Turnbull and Vonnegut [23] (Eq. (5)):

$$\Delta T = \frac{T_m E V_M}{-\Delta H} \cdot f^2 \quad (5)$$

where T_m is the melting temperature of the nucleating phase, E is the modulus of elasticity of the material, V_M is the molar volume of the crystal and ΔH is the heat of fusion. The reduction of ΔT found after the introduction of NbB₂/Al₃Nb nuclei (Fig. 3) indicates that there is a low f between Nb-based substrates and the primary α -Al grains. Consequently, Nb-based substrates have high *Potency* which is corroborated by the suppression of the formation of columnar grains, henceforth of the CET, and the significant refinement of the grain size of the Al-Si alloys when NbB₂/Al₃Nb nuclei are present (Fig. 4).

The solidification of the Al-Si alloys is greatly influenced by the Si content as the grain size increases with it. Coarser grains are

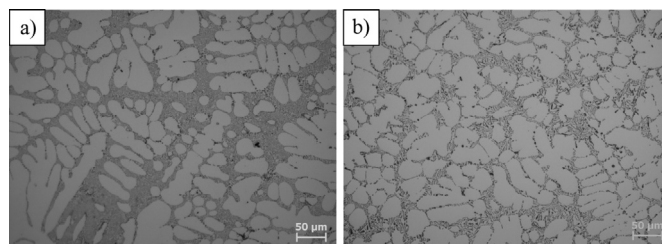


Fig. 6. Details of the distribution of the secondary eutectic Si phase in Al-Si alloys: (a) without (reference) and (b) with inoculation (NbB₂/Al₃Nb).

also obtained as the Q value increases in contrast with its intrinsic physical meaning. A higher growth restriction of the grains during solidification should lead to finer dendrites. However, the behaviour is consistent with literature for Al-Si alloys without and with the addition of Ti-based substrates [24,25]. Different theories have been proposed to explain it, such as change in solidification interval, change in solidification morphology and Si poisoning [20]. The addition of potent heterogeneous NbB₂/Al₃Nb nuclei makes the solidification of Al-Si alloys independent of Si content and Q as the grain size remains constant (Fig. 4).

During solidification Si is rejected by the growing grains up to the point that the remaining liquid reaches the eutectic composition and the eutectic phase nucleates and solidifies in between the arms of the primary α -Al dendrites. Therefore the reference Al-Si alloys develop a non-uniform distribution of the secondary eutectic phase confined between the dendritic arms of the coarse α -Al grains (Fig. 6a). After inoculation with Nb-based substrates the distribution of the eutectic phase is much more homogeneous (Fig. 6b). This is a consequence of the refinement of the primary α -Al dendritic grains whose greater number and smaller size leads to a more uniform distribution of the secondary eutectic Si in the cast structure [11,12].

Considering the eutectic nucleation, the reference alloys are characterised by relatively high T_g where it is well known that its magnitude is directly related to the level of modification [19]. The reduction of ΔT_{eu} after inoculation (Table 1) is due to the evaporation and loss of Sr upon remelting of the commercial Al-Si alloys and possibly some mutual poisoning between Sr and B [26] as the Al-Nb-B master alloy is supposed to have a hyper-stoichiometric composition.

Considering the effect of the solidification time (Fig. 5), for the reference Al-Si alloys solidification is mainly governed by heat extraction and grain growth. Consequently, the grain size is greatly influenced by the Si content or the equivalent superheating, as the alloys were cast at constant temperature, for instance $740 \pm 3^\circ\text{C}$. Consistently with the results of Fig. 4, the grain size of the inoculated alloys is far less dependent on the Si content. Furthermore, the grain size is not so greatly influenced by the solidification conditions due to the presence of NbB₂/Al₃Nb nuclei.

This is because the potent engineered heterogeneous nuclei promote nucleation over growth, the two stage of the solidification process, and thus solidification is less dependent on heat extraction and grain growth.

The better control of the solidification phenomena of Al-Si alloy achievable through the inoculation with Nb-based substrates opens up the possibility to design structural engineered components with homogeneous and enhanced performances. These can be mechanical (such as yield and ultimate tensile strength or ductility) and technological (better fluidity and filling capacity) or physical (soundness of the casting due to smaller, fewer and more homogeneous distributed microporosity). The inoculation of Al-Si alloy with engineered heterogeneous nuclei should lead to a more efficient, less expensive and less polluting production of lightweight

structural components such as engine blocks and wheels for the transportation sector.

5. Conclusions

In this study we demonstrated that stable Nb-based compounds ($\text{NbB}_2/\text{Al}_3\text{Nb}$) can successfully be produced in the form of Al-Nb-B master alloys. $\text{NbB}_2/\text{Al}_3\text{Nb}$ substrates are potent heterogeneous nuclei for engineering the solidification of cast Al-Si alloys. The Potency of the $\text{NbB}_2/\text{Al}_3\text{Nb}$ nuclei is reflected by the reduction of the undercooling needed to initiate the nucleation of the primary phase (i.e. α -Al dendrites) due to the low lattice mismatch. We also demonstrated that the introduction of engineered $\text{NbB}_2/\text{Al}_3\text{Nb}$ nuclei prior solidification effectively promotes nucleation over growth in Al-Si alloys. This makes the cast structure less dependent on the nature of the alloy, like Si content or growth restriction factor, and solidification conditions such as superheating and solidification time. Therefore, the resulting grains are much finer and the formation of columnar grains is prevented. Refinement of the secondary eutectic Si phases is also achieved due to the more uniform distribution of finer primary α -Al dendrites. The method is an effective and reliable practise to obtain Al-Si castings with more isotropic behaviour.

Conflict of interest

The authors declare no conflict of interest.

Acknowledgments

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.

References

- [1] I.J. Polmear, *Light Alloys. From Traditional Alloys to Nanocrystals*, 4th ed., Butterworth-Heinemann, UK, 2006.
- [2] N. Hari Babu, Y. Shi, K. Iida, D.A. Cardwell, A practical route for the fabrication of large single-crystal (RE)-Ba-Cu-O superconductors, *Nat. Mater.* 4 (2005) 476–480.
- [3] G.K. Sigworth, The grain refining of aluminum and phase relationships in the Al-Ti-B system, *Metall. Trans. A* 15 (2) (1984) 277–282.
- [4] M.M. Guzowski, G.K. Sigworth, D.A. Sentner, The role of boron in the grain refinement of aluminum with titanium, *Metall. Trans. A* 18 (1987) 603–619.
- [5] J.F. Grandfield, D.G. Eskin, I.F. Bainbridge, *Direct-Chill Casting of Light Alloys*, Wiley, NJ, 2013, pp. 149–155.
- [6] M. Easton, D.H. St. John, Grain refinement of aluminum alloys: part I. The nucleant and solute paradigms – a review of the literature, *Metall. Mater. Trans. A* 30 (6) (1999) 1613–1623.
- [7] M. Easton, D. St. John, An analysis of the relationship between grain size, solute content and the potency and number density of nucleant particles, *Metall. Trans. A* 36 (7) (2005) 1911–1920.
- [8] J.A. Spittle, S. Sadli, Effect of alloy variables on grain refinement of binary aluminium alloys with Al-Ti-B, *Mater. Sci. Technol.* 11 (1995) 533–537.
- [9] Y. Birol, AlB₃ master alloy to grain refine AlSi10Mg and AlSi12Cu aluminium foundry alloys, *J. Alloys Compd.* 513 (2012) 150–153.
- [10] Y. Birol, Performance of AlTi5B1, AlTi3B3 and AlB3 master alloys in refining grain structure of aluminium foundry alloys, *Mater. Sci. Technol.* 28 (4) (2012) 481–486.
- [11] M. Nowak, L. Bolzoni, N. Hari Babu, Grain refinement of Al-Si alloys by Nb-B inoculation. Part I: concept development and effect on binary alloys, *Mater. Des.* 66 (2015) 366–375.
- [12] L. Bolzoni, M. Nowak, N. Hari Babu, Grain refinement of Al-Si alloys by Nb-B inoculation. Part II: application to commercial alloys, *Mater. Des.* 66 (2015) 376–383.
- [13] J.C. Zhao, M.R. Jackson, L.A. Peluso, Mapping of the Nb-Ti-Si phase diagram using diffusion multiples, *Mater. Sci. Eng. A* 372 (1–2) (2004) 21–27.
- [14] C.-P. Reipt, G. Sauthoit, Deformation behaviour of the intermetallic phase Al₃Nb with DO₂₂ structure and of the Al₃Nb-base alloys. Part I: physical properties and short-term behaviour, *Intermetallics* 3 (1993) 159–169.
- [15] C.-P. Reipt, G. Sauthoit, Deformation behaviour of the intermetallic phase Al₃Nb with DO₂₂ structure and of the Al₃Nb-base alloys. Part II: creep behaviour, *Intermetallics* 4 (1996) 377–385.
- [16] I.R. Shein, A.L. Ivanovskii, Band structure of ZrB₂, VB₂, NbB₂ and TaB₂ hexagonal diborides: comparison with superconducting MgB₂, *Phys. Solid State* 44 (10) (2002) 1833–1839.
- [17] P. Schumacher, B.J. McKay, TEM investigation of heterogeneous nucleation mechanisms in Al-Si alloys, *J. Non-Cryst. Solids* 317 (2003) 123–128.
- [18] M. Schwarz, A. Karma, K. Eckler, D.M. Herlach, Physical mechanism of grain refinement in solidification of undercooled melts, *Phys. Rev. Lett.* 73 (10) (1994) 1380–1383.
- [19] M. Djurdjevic, H. Jiang, J. Sokolowski, On-line prediction of aluminum-silicon eutectic modification level using thermal analysis, *Mater. Charact.* 46 (1) (2001) 31–38.
- [20] J.A. Spittle, Grain refinement in shape casting of aluminium alloys – part I, *FTJ* (2008) 308–314.
- [21] I. Barin, *Thermochemical Data of Pure Substances*, VCH, Weinheim, Germany, 1993.
- [22] B.S. Murty, S.A. Kori, M. Chakraborty, Grain refinement of aluminium and its alloys by heterogeneous nucleation and alloying, *Int. Mater. Rev.* 47 (1) (2002) 3–29.
- [23] D. Turnbull, B. Vonnegut, Nucleation catalysis, *Ind. Eng. Chem.* 44 (1952) 1292–1298.
- [24] M. Abdel-Reihim, N. Hess, W. Reif, M.E.J. Birch, Effect of solute content on the grain refinement of binary alloys, *J. Mater. Sci.* 22 (1) (1987) 213–218.
- [25] L. Bäckerud, M. Johnsson, The relative importance of nucleation and growth mechanisms to control grain size in various aluminium alloys, *Light Met.* (1996) 679–685.
- [26] H. Liao, G. Sun, Mutual poisoning effect between Sr and B in Al-Si casting alloys, *Scr. Mater.* 48 (8) (2003) 1035–1039.