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Nb-based heterogeneous nuclei for enhanced α-Mg nucleation in Mg (-Al) alloys

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ABSTRACT

The effect of the introduction of in-situ formed Nb-based compounds on Al-including Mg alloys has been investigated. It is found that grain refinement is consistently achieved. Nb-based intermetallic particles are responsible of the effective heterogeneous nucleation of Al-including Mg alloys. The refining mechanism is discussed on the base of crystallography.

1. Introduction

Achievement of fine grain structure is highly desirable due to the intrinsic advantages both in terms of mechanical performances and/or structural homogeneity of castings made out of metals. From basic thermodynamic applied to solidification, fine grain structure can be easily obtained using (extremely) fast cooling rates, such as in the case of high-pressure die casting (HPDC) products. Conversely, when slow cooling conditions cannot be avoided, such as in sand casting or direct-chill (DC) casting, coarse and less uniform structure are obtained unless engineered designed heterogeneous nuclei are present, either intentionally added or in-situ formed (native), in the alloy. Magnesium (Mg) alloys are becoming important materials for the automotive industry due to their lightweighting effect of structural components. Consequently, the grain refinement of these alloys is very important. A clear distinction has to be made whether dealing with Al-free or Al-including Mg alloys. The former can be efficiently refined by the addition of zirconium (Zr) and the topic has recently been reviewed [1]. The latter cannot be refined by Zr due to the poisoning effect of Al on Zr, i.e. formation of stable intermetallics ineffective for the nucleation of Mg grains. Alternative methods were proposed for the refinement of Al-including Mg alloys [2]. Their names and principles are: 1) Elfinal process (addition of $FeCl_3$ to have Fe particles to act as nucleation sites), 2) refinement by impurity level control (native nucleation not completely understood), 3) superheating (heating of the melt at temperature much higher than the liquidus for short period of time), 4) carbon inoculation (formation of Al-carbides which promote the nucleation) and 5) employment of additives (Sr, Si, B, Ti and Ca are example of chemical elements studied) [3–5]. Nonetheless, a suitable grain refiner (i.e. reliable and easy to apply) for Al-including Mg alloys is still missing and none of the approaches discussed has been satisfactory in commercial use [6]. The aim of this work is to gain knowledge on the refinement of Al-including Mg alloys by means of inoculation with Nb-based compounds which act as stable heterogeneous nuclei during solidification.

2. Materials and methods

Inoculation of the melt was either performed by directly adding Nb powder and KBF_4 flux or via the employment of an appositively developed Al-4Nb-1B master alloy (i.e. equivalent to 5 wt% of stoichiometric NbB_2). The details of its production can be found in a previously published work where Al-xNb-yB master alloys were tested on Al(-Si) cast alloys [7]. Commercial AZ91D (Mg-9Al-1Zn) was melted inside a steel crucible at 690 °C under protective atmosphere ($SF6+N_2$). Melts without (reference) and with inoculation were cast into a permanent steel mould (cooling rate ~1 °C/s). Inoculation level was changed but the contact time was set to 30 min. The solidification process was monitored by thermal

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analysis. Grain size measurements were performed on polarised light micrographs of polished and etched samples.

3. Results and discussion

The grain refinement effect of Nb-B inoculation, using Nb powder and KBF_4 flux, on the AZ91D alloy is shown in Fig. 1. It is clear that the as-cast microstructure of both samples display a similar equiaxed dendritic structure. Because the addition of Nb-B inoculants is the only variable changed in the process after casting of the samples shown in Fig. 1a, it is evinced that Nb-inoculants are the responsible for the grain refinement observed in Fig. 1b.

When Nb powder and KBF_4 flux are added to the molten Al-including Mg alloys, different metallic borides can, actually, form:

$$2KBF_4 + Nb \rightarrow NbB_2 + 2KF_4 \tag{1}$$

$$2KBF_4 + 4Mg \rightarrow 2KMgF_3 + MgF_2 + MgB_2 \tag{2}$$

$$2KBF_4 + 3Al \rightarrow AlB_2 + 2KAlF_4 \tag{3}$$

Nevertheless, formation of NbB_2 intermetallic particles over Mg- or Al-intermetallic borides is thermodynamically more favourable being the enthalpy of formation -251 kJ/mol^{-1}, -156 kJ/mol^{-1} and -151 kJ/mol^{-1} for NbB_2, MgB_2 and AlB_2, respectively [8,9]. These same chemical reactions and principles are valid in the case of the Al-4Nb-1B master alloy although in the case Nb aluminides are also present. It is known that solute Al refines pure Mg, but increasing the Al content above 5 wt% does not produce any further significant refinement of the grain size [6]. The grain refinement performance of the Al-4Nb-1B master alloy on the AZ91D alloy is compared with other grain refiners (i.e. data about inoculation available in the literature [10–13]) in Fig. 2. It is worth mentioning that the most similar casting conditions were chosen for the comparison although not always the same exact solidification conditions (i.e. pouring temperature or cooling rate) were available.

The initial addition of 0.05 wt% NbB_2 via Al-4Nb-1B master alloy to the AZ91D induces a rapid reduction of the grain size. Little further refinement is then obtained with supplementary addition of master alloy and the grain size stabilises around 200 μm. The results obtained are consistent with the data available in the literature about Al-5Ti-1B or carbon inoculation of the AZ91D alloy [10–13]. Actually, it can be noticed that there is quite a significant influence from the nature of the source used to introduce carbon into the melt, which is the main reason preventing

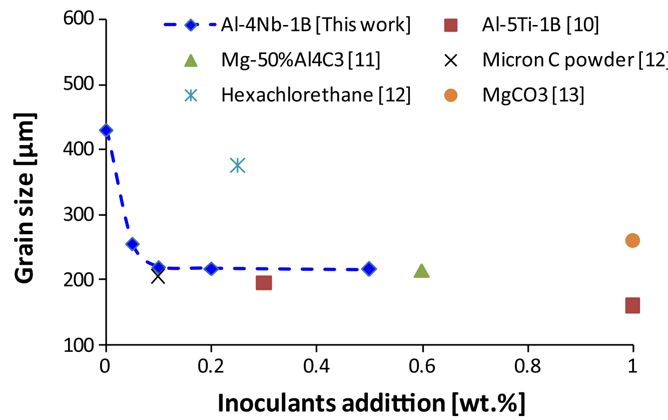

Fig. 2. Grain size of the AZ91D alloy as a function of different inoculants [Pouring T~650 °C].

the industrial employment of this refining practise.

The potency of Nb-B inoculants as heterogeneous substrate for the nucleation of primary α-Mg can be demonstrated by crystallography. The free energy at the nucleating interface is definitely an important factor controlling the nucleation process. Nevertheless, an analysis of the process on the base of such energy is rather complicated because of the many contributing aspects. Instead, the model proposed by Bramfitt in the nineteen seventies is conventionally used to evaluate the potency of heterogeneous nuclei on the base of crystallographic matching where the lattice mismatch or misfit (Ψ) is calculates as per [14]:

$$\Psi_{(hkl)_n}^{(hkl)_s} = \sum_{i=1}^{3} \frac{\frac{\left|(d_{[uvw]_s^i} \cos\theta) - d_{[uvw]_n^i}\right|}{d_{[uvw]_n^i}}}{3} \tag{4}$$

where (hkl) and $[uvw]$ are low-index plane and direction of the nucleating phase (n) or substrate (s), respectively, and θ is the angle between a pair of low-index directions $[uvw]$ on the (hkl) plane. Bramfitt's model is, actually, a development of the original model of Turnbull and Vonnegut [15] where (Ψ) was assessed as the ratio between the average difference in lattice constants (Δa) of low index planes of the nucleating phase and the substrate and the lattice parameter (a_0) of the nucleating phase:

$$\Psi = \Delta a / a_0 \tag{5}$$

The model was developed on the fact that the energy barrier to heterogeneous nucleation is only due to the structural aspects of

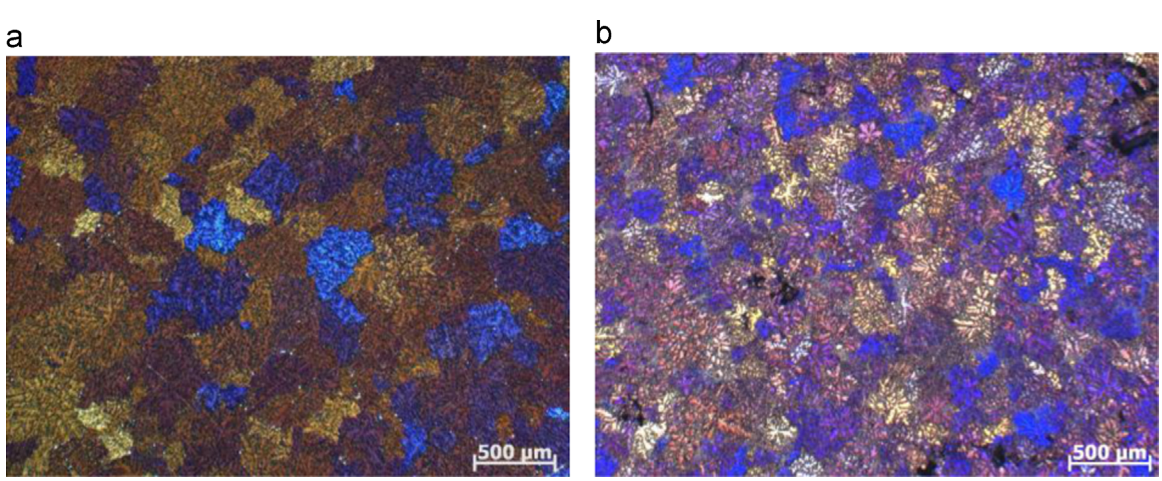

Fig. 1. Polarised light optical micrographs of the grain size of the AZ91D alloy: a) reference and b) Nb-B inoculated.

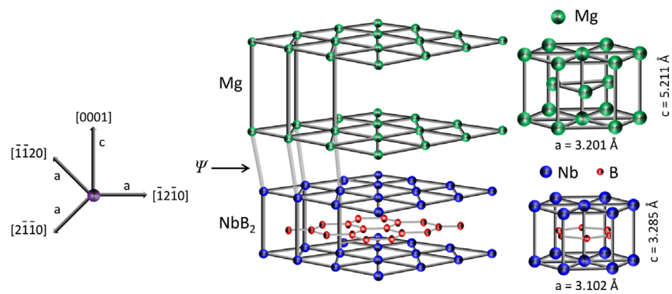

Fig. 3. Sketch of the Mg and NbB_2 hexagonal crystal structure and the low lattice misfit along their (0001) basal plane.

the nucleating phase/substrate interface if their chemical parameters are comparable. Consequently, this energy reaches its minimum value for coherent interfaces. It is worth mentioning that this simple approach is only valid in systems with isomorphous structures or whether the nucleating phase and the substrates are characterised by the atomic configuration along certain low index planes. NbB_2 and Mg share similar hexagonal crystal lattice structure and *a* lattice constant where along the (0001) basal plane $\Psi \sim 0.03$. The low lattice misfit along this particular low index plane, which is schematically represented in Fig. 3, is actually believed to promote the nucleation of the primary α-Mg dendritic grains.

Further proves that the low lattice mismatch of the Nb-B inoculants is responsible for the refinement of the structure of the Al-including Mg alloys derives from solidification curves. The original model proposed by Turnbull and Vonnegut [15] is once again suitable because it states that $\Delta T \propto \Psi^2$. Therefore, the lower the lattice misfit between the substrate and the nucleating phase the lower the undercooling needed for nucleation. Ultimately, the undercooling values obtained as the difference between the maximum and minimum of the nucleation peak of the solidification curves were approximately 0.90 K and 0.16 K for the AZ91D without and with Nb-B inoculation, respectively.

4. Conclusions

The grain refining efficacy of Nb-B inoculation in Al-including Mg alloys was experimentally investigated. It is found that Nb-based intermetallic particles act as heterogeneous nucleation substrates during the solidification of Mg. Because of this, significant grain size reduction is observed. The grain refining mechanism of NbB_2 compounds has been proposed. Crystallographic, thermodynamics and chemical data support the suggested refining mechanism. Models available in the literature were used to assess the crystal structure misfit between the nucleating Mg and NbB_2 intermetallics. From the low planar mismatch ($\Psi \sim 0.03$), it is believed that NbB_2 are potent heterogeneous sites for the formation of dendritic primary α-Mg grains. A novel Al-4Nb-1B master alloy is proposed and its efficacy as refiner of Al-including Mg alloy asserted.

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