Trans Indian Inst Met (2018) 71(11):2771–2775
https://doi.org/10.1007/s12666-018-1435-4

TECHNICAL PAPER

Prediction and Verification of Effective Grain Refiners for Magnesium Alloys

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Received: 18 July 2018 / Accepted: 12 September 2018 / Published online: 12 October 2018

Abstract Magnesium alloys are important lightweight materials, enabling improved fuel efficiency and reduced emissions in automotive and aerospace industries. Heterogeneous nucleation and effective grain growth restriction during the solidification of these alloys result in enhanced mechanical properties. These can be achieved via the addition of suitable inoculants to the alloy, yet the selection of a potent grain refiner is often challenging and is, therefore, the subject of much research. Mathematical models can be used for the identification and development of effective refiners, subject to appropriate validation. This study examines the grain-refining efficiency of innovative magnesium inoculants via lattice disregistry calculations and presents experimental verification for the models in permanent mould castings.

Keywords Magnesium · Grain Refinement · Casting · Crystallography

1 Introduction

The need for high-performance and lightweight engineering materials in the automotive and aerospace sector is rapidly increasing. Due to the continuous rise in energy costs, automobile manufacturers are constantly striving to reduce vehicle weight, improve fuel efficiency, decrease harmful emissions and improve material recyclability. Approximately 35% lighter than aluminium (Al) alloys, magnesium (Mg) alloys are suitable alternatives that offer high specific strength compared to conventional engineering alloys [1]. In addition, Mg alloys have good damping capacity, excellent castability and good machinability, enabling them to meet the demands of the industries. However, only a minor proportion of the current average vehicle weight is comprised of Mg alloys, primarily since they exhibit lower yield strength and ultimate tensile strength compared to Al and iron-based components [1]. The strength and ductility of Mg alloys must be improved to ensure their viability as a replacement for other alloys.

Enhanced quality of polycrystalline castings can be attained via grain refinement. A fine grain size usually leads to increased strength, ductility and a uniform distribution of secondary phase. Typically, this can be achieved by the addition of effective inoculants to the melt prior to solidification, which promotes heterogeneous nucleation of the matrix phase [2]. Although some grain refiner systems, such as Al–Ti–C, Al–Ti–B and Al–Ti, have found much success when added to Al alloys, a universal and highly effective refiner for Mg alloys is still elusive [3–5]. To date, zirconium (Zr) has been reported to be one of the more effective inoculants for Al-free cast Mg alloys [6–9]. However, Zr is not an efficient grain refiner for Mg alloys containing Al, such as the most widely used commercial Mg alloy AZ91 [10]. Therefore, considerable effort has been devoted in identifying an alternative inoculant that can efficiently refine both Al-free and Mg–Al alloys.

The use of crystallographic models is useful for the prediction of effective grain refiners prior to expensive and tedious experimentation. These models, including the Turnbull and Vonnegut model [11] and the Bramfitt model [12], rely on the notion that a potent nucleant requires good crystallographic matching with the host material in order to reduce the interfacial energy between the inoculant and the

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host matrix. Nevertheless, all models depend on experimental verification across various alloy systems to ensure their validity.

For the first time, this study applies the Bramfitt model to predict the effectiveness of TiB_2, SiC and TiC particles in the grain refinement of Mg alloys, and compares the results to experimental findings. The lattice disregistry between the inoculants and the host matrix as well as the associated effects on grain size and microstructure of the cast alloys has been examined. This enabled an evaluation of the suitability of the model, given several important issues that may arise in alloy systems.

2 Materials and Methods

From a crystallographic perspective, an effective inoculant must have suitable lattice matching with the host matrix. Therefore, the degree of disregistry between the two phases is typically used as a measure for grain-refining potential. In this study, the plane-to-plane matching (P2PM) model, proposed by Bramfitt [12], has been used to predict the effectiveness of inoculants. This model compares the interatomic spacings and the close-packed directions of pairs of low-index close-packed planes between the inoculant and the host metal within a 90° quadrant:

$$\delta_{(hkl)_n}^{(hkl)_s} = \frac{1}{3}\sum_{i=1}^{3}\frac{\left|d_{[uvw]_s^i}\cos\theta - d_{[uvw]_n^i}\right|}{d_{[uvw]_n^i}} \times 100 \qquad (1)$$

where n and s denote the matrix (nucleus) and the inoculant (substrate), respectively, d is the interatomic spacing along $[uvw]$, (hkl) is a low-index close-packed plane, $[uvw]$ is a low-index direction on the (hkl) plane, and θ is the angle between a pair of adjacent low-index directions on the (hkl) planes.

From his study, Bramfitt concluded that disregistry values below 12% indicate good potential and values below 6% indicate very good potential for refinement.

3 Results

Figure 1 displays the low-index close-packed planes for Mg, SiC, TiC and TiB_2 that were chosen for crystallographic analysis. The figure also illustrates the chosen low-index directions and the angles between the directions. Magnesium, SiC and TiB_2 had hexagonal crystal structures with lattice parameters of a = 0.321 nm and c = 0.521 nm for Mg [13], a = 0.308 nm and c = 1.51 nm for SiC [14] and a = 0.304 nm and c = 0.324 nm for TiB_2 [15]. In contrast, TiC had a cubic structure with a lattice constant of a = 0.433 nm [16].

The disregistry value for the SiC-Mg system with a $(0001)_{SiC}\|(10\bar{1}0)_{Mg}$ orientation relationship was determined to be 2.35%. This was done by applying the P2PM model to the (0001) basal plane of SiC and the $(10\bar{1}0)$ prismatic plane of Mg. The low-index directions chosen for SiC were $[\bar{1}100]$, $[\bar{1}2\bar{1}0]$ and $[11\bar{2}0]$ with interatomic spacings of 0.534 nm, 0.616 nm and 0.308 nm, respectively. Similarly, the low-index directions chosen for Mg were [0001], $[11\bar{2}3]$ and $[11\bar{2}0]$ with interatomic spacings of 0.521 nm, 0.612 nm and 0.321 nm, respectively. An angular difference of 1.64°, between the direction for SiC and the direction for Mg, was observed. Additionally, the $(0001)_{SiC}\|(0001)_{Mg}$ was also considered as a viable orientation relationship; however, the resultant disregistry was not as favourable as the $(0001)_{SiC}\|(10\bar{1}0)_{Mg}$ orientation.

Similar to SiC, the planar disregistry of the TiC–Mg system with a $(111)_{TiC}\|(0001)_{Mg}$ orientation relationship was calculated using the P2PM model. The resultant disregistry, between the (111) plane for TiC and the (0001) plane for Mg, was 4.67%. The low-index directions chosen for TiC were $[\bar{1}\bar{1}1]$, $[\bar{1}01]$ and $[\bar{1}10]$ with interatomic spacings of 0.530 nm, 0.306 nm and 0.306 nm. Likewise, the low-index directions chosen for Mg were $[\bar{1}100]$, $[\bar{1}2\bar{1}0]$ and $[11\bar{2}0]$ with interatomic spacings of 0.556 nm, 0.321 nm and 0.321 nm.

The disregistry for the TiB_2–Mg system with $(0001)_{TiB_2}\|(0001)_{Mg}$ orientation relationship was calculated to be 5.27%. This was done by matching the (0001) plane of TiB_2 to the (0001) plane of Mg. The low-index directions used for evaluation on the (0001) plane for both TiB_2 and Mg were $[\bar{1}100]$, $[\bar{1}2\bar{1}0]$ and $[11\bar{2}0]$ with interatomic spacings of 0.527 nm, 0.304 nm and 0.304 nm for TiB_2 and 0.556 nm, 0.321 nm and 0.321 nm for Mg. In addition, the $(0002)_{TiB_2}\|(0001)_{Mg}$ orientation was also determined to be feasible; however, the $(0001)_{TiB_2}\|(0001)_{Mg}$ orientation resulted in a lower disregistry value.

A summary of the low-index directions, interatomic spacings and resultant planar disregistry values of the possible orientation relationships between Mg and SiC, TiC and TiB_2 at ambient temperature is shown in Table 1. All three inoculant-matrix systems fall within the very effective range (< 6%); therefore, it is theoretically likely for Mg grains to nucleate on these substrates based on the selected orientation relationships.

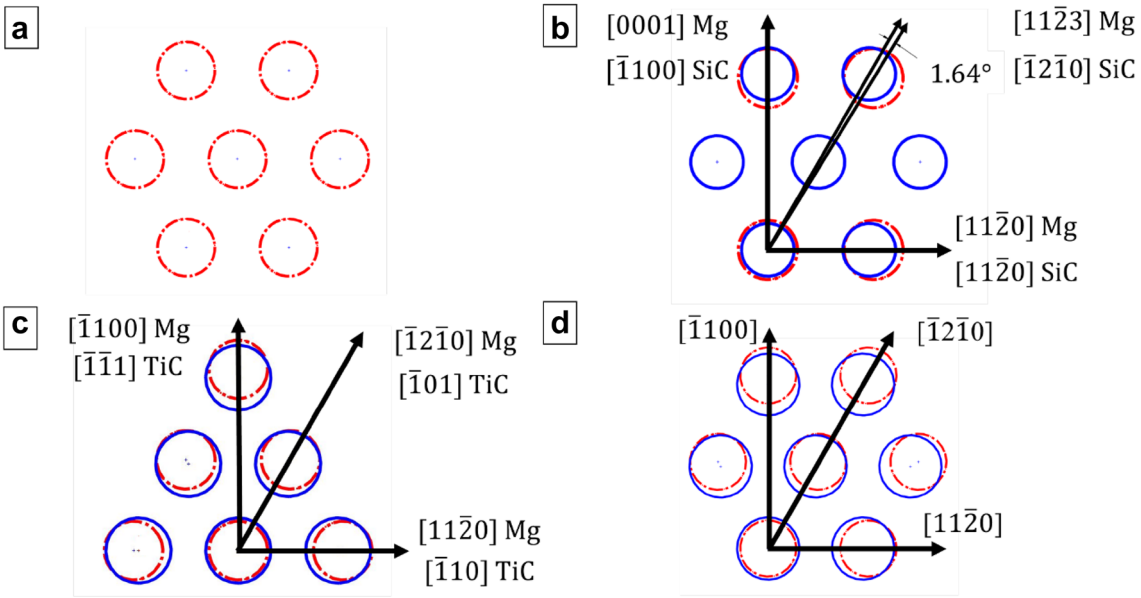

Fig. 1 **a** (**0001**) plane of Mg (red-dashed), **b** (**0001**) plane of SiC (blue-solid) and (**1010**) plane of Mg (red-dashed), **c** (**111**) plane for TiC (blue-solid) and (**0001**) plane for Mg (red-dashed) and **d** (**0001**) plane of TiB_2 (blue-solid) and (**0001**) for Mg (red-dashed) (color figure online)

Table 1 Calculated planar disregistry values for $(\mathbf{0001})_{SiC}\|(\mathbf{10\bar{1}0})_{Mg}$, $(\mathbf{111})_{TiC}\|(\mathbf{0001})_{Mg}$ and $(\mathbf{0001})_{TiB_2}\|(\mathbf{0001})_{Mg}$ orientation relationships at ambient temperature

	$(0001)_{SiC}\|(10\bar{1}0)_{Mg}$			$(111)_{TiC}\|(0001)_{Mg}$			$(0001)_{TiB_2}\|(0001)_{Mg}$		
$[uvw]_s$	[$\bar{1}$100]	[$\bar{1}$2$\bar{1}$0]	[11$\bar{2}$0]	[$\bar{1}\bar{1}$1]	[$\bar{1}$01]	[$\bar{1}$10]	[$\bar{1}$100]	[$\bar{1}$2$\bar{1}$0]	[11$\bar{2}$0]
$[uvw]_n$	[0001]	[11$\bar{2}$3]	[11$\bar{2}$0]	[$\bar{1}$100]	[$\bar{1}$2$\bar{1}$0]	[11$\bar{2}$0]	[$\bar{1}$100]	[$\bar{1}$2$\bar{1}$0]	[11$\bar{2}$0]
$d[uvw]_s$ (nm)	0.534	0.616	0.308	0.530	0.306	0.306	0.527	0.304	0.304
$d[uvw]_n$ (nm)	0.521	0.612	0.321	0.556	0.321	0.321	0.556	0.321	0.321
θ	0	1.64	0	0	0	0	0	0	0
δ		2.35			4.67			5.27	

4 Discussion

The three inoculants indicated above have been studied experimentally by various researchers. This section presents their findings and addresses several important details and potential issues that may arise in the use of the crystallographic model for refiner prediction.

4.1 Chemical Stability

Silicon carbide has exceedingly close lattice matching with Mg (2.35%), and therefore, it has been the subject of several investigations. However, suitable lattice mismatch is not sufficient for effective grain refinement. An issue that is commonly overlooked in inoculant selection is chemical stability. Prior to addition, it must be confirmed that the chosen grain refiner is chemically stable within the host melt. Otherwise, the inoculant particles may form reaction products that decrease the mechanical properties or reduce the effectiveness of other elements in solution that provide grain growth restriction.

This can be illustrated through the results of Chen et al. [17], who investigated the effect of SiC addition to AZ91D alloy using permanent mould casting and mechanical stirring. They presented that the optimal SiC addition level was 0.2 wt%, which decreased the grain size from 311 to 71 μm (77% reduction). However, while determining the mechanism of refinement, they discovered that treatment with these particles led to the development of two phases: a Chinese-script type Mg_2Si phase and a blocky-type Al_4C_3 phase. These new phases were suggested to form through the SiC and Al reaction as follows:

$$3SiC + 4Al \rightarrow Al_4C_3 + 3Si \quad (2)$$

$$2Si + Mg \rightarrow Mg_2Si \quad (3)$$

Thus, despite crystallographic suitability, the unstable SiC particles did not act as heterogeneous nucleation sites, as they were removed from the melt. As well, Al was removed from solution, which might have led to grain coarsening and reduced mechanical properties [13]. Furthermore, the researchers determined crystallographically that Mg_2Si could not act as a nucleant for Mg. Therefore, they suggested Al_4C_3 as the only remaining compound for nucleation. Guo et al. [18] examined the effectiveness of Al_4C_3 substrates as heterogeneous nucleation sites for Mg. They calculated that the $(10\bar{1}0)_{Al_4C_3}\|(10\bar{1}0)_{Mg}$ orientation relationship resulted in a disregistry of 3.35% between Mg and Al_4C_3 which, fell into the very effective range and, thus, supported the results from Chen et al.

To summarize, although lattice matching provides an indication of grain-refining efficiency, it is not the sole characteristic of an effective inoculant. Prior to inoculation, one must examine the stability of potential grain refiners in the host matrix to avoid detrimental reaction products.

4.2 Dissimilar Crystal Structures

Unlike SiC, which has a hexagonal crystal structure, TiC crystallizes in a cubic NaCl-type structure with four formula units per cell and a lattice parameter of a = 0.433 nm [16]. The planar disregistry of the $(111)_{TiC}\|(0001)_{Mg}$ system has been calculated to be 4.67% (Table 1), which falls into the very effective category. Therefore, experimental validation of this inoculant-matrix system is warranted.

Since Mg and TiC do not have similar crystal structures, if traditional linear disregistry models (e.g. the Turnbull and Vonnegut model [11]) are used to examine the effectiveness of TiC substrates for nucleating Mg, the resultant disregistry will be 35%. This result suggests poor lattice matching, since linear disregistry models only compare the lattice parameters between inoculant-matrix systems, with no regard towards atomic arrangement within their close-packed planes. This illustrates the inherent limitations of linear disregistry models in comparison to the P2PM model for predicting the nucleating potential of phases with differing atomic arrangements.

Several studies have been performed to validate the effectiveness of TiC, as a nucleant for Mg. Zhang et al. [19] investigated the effect of TiC in AZ91 using an in situ synthesis approach by the addition of sintered Al, Ti and graphite blocks. They found that the TiC particles formed led to a visible decrease in grain size, but the exact values were not published. The decrease in grain size was attributed to the nucleation of Mg crystals from the TiC substrates and the subsequent growth of the new crystals. Zhang et al. also suggested that TiC particulates around the grain boundaries reduced the growth rate of the primary Mg phase, which allowed the melt sufficient time to generate more nuclei. Therefore, a combination of increased heterogeneous nucleation and grain growth restriction was the cause of the reduced grain size.

Based on the results of Zhang et al., it can be concluded that TiC is indeed an efficient refiner for Mg. However, these results could not be predicted by using a linear disregistry model. Therefore, in order to predict the effectiveness of inoculant-matrix systems with differing atomic arrangements, a planar disregistry model, such as the P2PM model, must be utilized.

4.3 Secondary Phase Nucleation

Titanium diboride particles are often used to refine Al alloys because of their high hardness (33 GPa), low density (4.451 g/cm^3), high melting point (2790 °C) and high modulus (530 GPa) [20, 21]. As indicated by the calculated lattice disregistry above, TiB_2 is potentially a good candidate for Mg grain refinement as well.

Prior to grain refinement, one must consider the nucleating potential of the inoculant not only for the alloy host matrix, but also for the secondary phases that forms during solidification. For example, in case of AZ91 Mg alloy, which consists primarily of Mg, Al, zinc (Zn) and manganese (Mn), HCP-structured Al–Mn intermetallics are often observed. These phases are typically evenly distributed throughout the microstructure. However, if sufficient lattice matching exists between the intermetallic and the inoculant, the Al–Mn phase may segregate to the refiner particles. Crystallographically, the lattice parameter of the Al–Mn phase (a = 0.2697 nm [22]) matches closely to TiB_2 (a = 0.304 nm). According to the P2PM model, Al–Mn intermetallics have good lattice matching (11.18% disregistry) with TiB_2, indicating a possible preferential precipitation on the inoculant particles rather than on the Mg phase. It is therefore possible that the TiB_2 particles can act as nucleating sites for Al–Mn intermetallics, resulting in their inhomogeneous distribution within the Mg matrix and reducing the mechanical properties of the alloy. Nonetheless, this phenomenon has not been found by researchers investigating the effects of TiB_2 in Mg melts.

There are several studies that have investigated the effects of TiB_2 particles on Mg alloys, either isolated or in master alloys. The research usually reports success in the refinement of the Mg grains with little mention of any influence on the secondary phase distribution. For example, Elsayed et al. [23] examined the effect of Al–5Ti–1B and Al–5Ti–3B master alloys on the grain size of AZ91E Mg alloy. The researchers observed that the optimal addition level of Al–5Ti–1B was 0.1 wt%, which led to a decrease in grain size from 1000 to 323 μm (68% decrease). This result was attributed to TiB_2 particles that was formed in situ and acted as both heterogeneous nucleation sites and

grain growth restrictors. Similarly, they observed that the ideal addition level of the Al–5Ti–3B refiner was 1.0 wt%, which decreased the grain size from 1000 to 361 μm (64% reduction). Elsayed et al. suggested that the addition of Al–5Ti–3B led to the formation of TiB_2 as well as AlB_2 particles, and both acted as heterogeneous nucleation sites for the Mg crystals. According to Suresh et al. [24], AlB_2 has an HCP structure with lattice parameters of $a = 0.301$ nm and $c = 0.325$ nm, which are very similar to that of Mg. Suresh et al. calculated the disregistry between AlB_2 and Mg to be 6.09%, which is slightly above the very effective range. Hence, it is the authors' opinion that in the study by Elsayed et al., some of the more potent TiB_2 particles have got replaced by less effective AlB_2 particles, which may have led to the slightly coarser grain sizes. Further investigation is required to validate this hypothesis.

Although no evidence of secondary phase segregation was found in the study performed by Elsayed et al., preferential nucleation is still possible given sufficient lattice matching. Thus, in the selection of an inoculant, it is suggested that the crystallography of all phases in the microstructure should be evaluated.

5 Conclusion

The lattice disregistry between Mg and SiC, TiC and TiB_2 substrates was calculated using the planar disregistry model proposed by Bramfitt as 2.35%, 4.67% and 5.27%, respectively. The disregistry values were then compared to experimental results from the literature. The following conclusions could be drawn from this study:

1. The planar disregistry model is a simple and effective method for choosing potential inoculants. Although the model does not take into consideration all the factors that lead to a potent nucleant, it can aid in selecting potential candidates in a quick and efficient manner.
2. The chemical stability of an identified potential refiner in the host matrix must be examined prior to inoculation to avoid detrimental reaction products.
3. The P2PM model overcomes the one-dimensional limitations of linear disregistry models. Hence, it is effective in predicting the nucleating potential of matrix-substrate combinations with dissimilar atomic arrangements.
4. Inhomogeneous secondary phase distribution is known to hinder mechanical properties. If adequate lattice matching exists between an inoculant and a secondary phase, preferential nucleation of the secondary phase on the inoculant may be possible. Further research is required to experimentally verify this possibility.

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