The grain refinement mechanism of cast aluminium by zirconium

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Abstract

The mechanism underlying the grain refinement of cast aluminium by zirconium has been studied through examination of a range of Al alloys with increasing Zr contents. Pro-peritectic Al_3Zr particles are reproducibly identified at or near the grain centres in grain-refined alloy samples based on the observations of optical microscopy, scanning electron microscopy and X-ray diffraction. From the crystallographic study using the edge-to-edge matching model, electron backscatter diffraction and transmission electron microscopy, it is substantiated that the Al_3Zr particles are highly potent nucleants for Al. In addition, the effects of Al_3Zr particle size and distribution on grain refinement has also been investigated. It has been found that the active Al_3Zr particles are bigger than previously reported other types of active particles, such as TiB_2 for heterogeneous nucleation in Al alloys. Considering the low growth restriction effect of Zr in Al (the maximum Q-value of Zr in Al is 1.0 K), it is suggested that the significant grain refinement of Al resulting from the addition of Zr can be mainly attributed to the heterogeneous nucleation facilitated by the in situ formed Al_3Zr particles.
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Keywords: Cast aluminium; Grain refinement; Peritectic; Edge-to-edge matching model

1. Introduction

The mechanism of grain refinement through inoculation in aluminium alloys has been studied for over half a century [1–4]. Although many theories/models [5–13] have been proposed, none of them can fully elucidate all of the observations from experiment and practice. In general, it is now accepted that the presence of both potent nucleant particles and sufficient solutes is essential for effective grain refinement [2,14–17]. Despite the common recognition of these two essentials, the details of the grain refinement mechanism(s) are still of some ambiguity. One of the major problems is to determine the exact factors that control the efficiency of grain refinement. For example, the recent investigations [18–22] on a number of newly developed grain refiners for Mg–Al-based alloys and Ti alloys showed

relatively low efficiencies compared to that expected from the crystallographic matching, which represents the potency of heterogeneous nucleation and the constitutional undercooling contribution of solute elements. Therefore, it appears that something important is still missing in the current understanding of grain refinement. It is worth noting that the spotlight of previous studies on grain refinement mechanism of Al alloys was primarily focused on the Al–Ti–B and Al–Ti–C systems as they are the most common grain refiners used in the foundry [3,4]. However, it is believed that the study of grain refinement resulting from other solute elements, which also produce effective grain refinement in Al may provide fresh insight into the factors that control the grain refining efficiency.

It has been long realized that peritectic systems are often associated with effective grain refinement of the parent metal, such as Al–Ti, Mg–Zr and Mg–Y–Al alloys [23–26]. However, the peritectic approach has been considered as incorrect because addition of far less Ti than its

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maximum solubility in Al can still produce significant grain refinement even though there is no peritectic reaction involved. This raises the question of whether a similar grain refining effect can be obtained in other peritectic systems. One of the typical examples of peritectics is the Al–Zr system, in which the addition of Zr produces appreciable grain refinement in Al. A number of researchers [7,23,24] have investigated the grain refinement of Al alloys by Zr and simply attributed the grain refinement to the peritectic reaction induced by the pro-peritectic Al$_3$Zr phase. Nevertheless, there is still lack of direct experimental evidence to confirm the effect of the peritectic reaction. In addition, it is noted that few of the researchers [7,27] studied the crystallography between the pro-peritectic Al$_3$Zr particle and the Al matrix, which has been considered to be of great significance in affecting grain refinement efficiency [25,28–30]. Thus, the detailed mechanism underlying the grain refinement is still beyond full understanding, particularly in terms of the aforementioned two essentials. The particular questions remaining are whether the observed efficiency of grain refinement by Zr is mainly related to the peritectic reaction induced by the pro-peritectic Al$_3$Zr phase (as proposed by previous researchers), whether it is due just to the nucleation potency of the pro-peritectic Al$_3$Zr particles that promote grain refinement via heterogeneous nucleation, or both.

Recently, the grain refining effect on pure Al of a range of peritectic-forming solutes including Zr was re-examined by the authors and a Q-value model was used to elucidate the obtained grain refinement [31]. It was suggested that the considerable grain refinement resulting from the addition of Zr is probably due to the introduction of copious nucleant particles, which promote grain refinement via enhanced heterogeneous nucleation. However, little experimental evidence was provided. The present work aims to clarify the actual roles/effects of Zr addition on grain refinement of Al through (i) identification of the pro-peritectic Al$_3$Zr particles at grain centres by X-ray diffraction (XRD) and scanning electron microscopy (SEM); (ii) characterization of the crystallographic features between Al$_3$Zr and Al matrix using the edge-to-edge matching (E2EM) model [29,30,32–35] to evaluate the potency of Al$_3$Zr; and (iii) verification of the crystallographic matching using both electron backscatter diffraction (EBSD) and transmission electron microscopy (TEM). Then the mechanism of grain refinement of Al by Zr is discussed in terms of the nucleant potency, solute contribution, and size and distribution of the active Al$_3$Zr particles. Although the addition of Zr over the maximum solubility may adversely affect the mechanical properties of Al alloys, the present work is purely a theoretical study aiming to understand the mechanism of grain refinement in cast Al.

In the past decade, it has been demonstrated that the E2EM model is a powerful tool in understanding grain refining efficiency through calculation of crystallographic matching between inoculants and metal matrix. This model was originally developed by Zhang and Kelly [32–35] to predict the orientation relationships (ORs) and habit plane between adjacent phases arising from phase transformations in solids. Since the crystallographic characteristics between the nucleation substrate and metal matrix also play an important role in grain refinement, the E2EM model has been extended to the study of grain refinement and achieved great success in elucidating the mechanisms of grain refinement [29,30] and poisoning phenomena [36,37], evaluating the potency of current grain refiners [29,30,38] and discovering new and effective ones [26,27] in both Al and Mg alloys. The critical assumption of the E2EM model is that the crystallographic features between any two phases are governed by the minimization of interfacial energy, which corresponds to the maximum matching of parallel atomic rows across the interface between phases. In general, the matching rows should be close-packed (cp) or nearly cp atom rows with small interatomic spacing misfit (f_r) to maximize the atomic matching along the parallel rows. The matching rows can be either straight or zigzag, but the model requires that straight rows match with straight rows while zigzag rows match with zigzag rows. Such rows are termed *matching directions*. In addition, the pair of matching directions should also be contained in a pair of cp or nearly cp planes which have a small interplanar spacing misfit (f_d). Such planes are termed *matching planes*. If the values of f_r and f_d are sufficiently small (e.g. f_r and f_d both <10%) in a given system, an energetically favourable OR can be predicted and expressed in terms of the parallelism of the matching rows and near parallelism of the matching planes. The angular deviation between the matching planes and the orientation of the interface plane can be further determined by using the $\Delta\mathbf{g}$ parallelism criterion [39,40]. Following the precedent success, the present work will use the E2EM model to evaluate the crystallographic matching and then the potency of Al$_3$Zr in Al. The predications will then be verified by EBSD and TEM.

In addition to the crystallographic matching between the nucleant particles and matrix metal, the size of the nucleant particles also plays a crucial role in grain refinement, as can be well described using the free growth theory/model proposed by Greer and his co-workers [41–44]. The theory proposes that the onset of free growth of a nucleus on a nucleant particle is the controlling factor in grain initiation, and the critical undercooling for free growth to be reached is related to the nucleant particle size by the following equation:

$$\Delta T_{fg} = \frac{4\sigma}{\Delta S_V d} \tag{1}$$

where σ is the solid–liquid interfacial energy, ΔS_V is the entropy of fusion per unit volume and d is the characteristic size of the active nucleant particle, which is the disc diameter of a TiB$_2$ particle in their case studies [41–44]. Based on the free growth theory, considerable success has been achieved in predicting the grain size of Al alloys inoculated with commercial grain refiners and in understanding the mechanism that limits