Grain refinement of magnesium alloys by zirconium: Formation of equiaxed grains

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Abstract

Conical samples of a Mg–3.8%Zn–2.2%Ca alloy undergoing the columnar to equiaxed transition, induced by the addition of 1.5%Zr, have been examined. The zirconium contents in the equiaxed grains just ahead of the columnar front were found to generally vary between 0.2% and 0.3%. Further assessment confirmed that, as the first step towards optimum grain refinement, a zirconium content of 0.22% was necessary for the formation of equiaxed grains in the experimental alloy under conditions similar to sand casting.

1. Introduction

Magnesium alloys can be generally classified into two broad groups depending upon whether they are alloyed with aluminium: aluminium free and aluminium bearing. The aluminium free alloys mainly refer to those containing zirconium or those grain refined by zirconium. These are an important high value added class of alloys that are based on the exceptional grain refining ability of zirconium when added to these alloys.

The commercial practice of grain refinement of magnesium alloys with zirconium has been fundamentally based on the peritectic mechanism proposed by Emley [1]. Consequently, the zirconium content dissolved in the melt needed to be greater than the peritectic composition, which was believed to be 0.601%Zr (in wt.%, and hereafter) according to the Mg–Zr phase diagrams established before 1998 [2]. As a result, the 0.6%Zr content naturally formed the basis for grain refinement of magnesium alloys with zirconium.

Recently, the solubility of zirconium in molten magnesium at the peritectic temperature has been reassessed to be 0.443% [3,4]. This is about 30% lower than the previous 0.601%Zr. Since about 1960, adding zirconium to magnesium has been achieved mainly through the use of Mg–Zr master alloys [5]. These are costly additives. In addition, because of the low alloying efficiency [5,6], an excess of zirconium needs to be introduced in order to achieve the full zirconium content for optimum grain refinement. For instance, when a Zirmax master alloy (Mg–33.3%Zr) is used, an addition of 7% of the master alloy, equivalent to adding 2.33%Zr, is necessary to ensure the 0.6%Zr content when starting from fresh pure magnesium ingots [1]. Therefore, if the 0.443%Zr solubility content can be established as a new basis for grain refinement with zirconium, it will help to reduce the cost of production of zirconium containing magnesium alloys. Recent work by Lee et al. [7] showed that small additions of zirconium (≤0.32%) could reduce the grain sizes of pure magnesium samples cast under fast cooling conditions, where a cubic mild steel mould (dimensions: 100 × 100 × 100 mm³) with a cylindrical cavity of 50 mm diameter, preheated to 200 °C, was used. The mechanism was attributed to the strong growth restriction effect of zirconium on magnesium.

The ultimate goal of grain refinement is to obtain a fine, uniform and equiaxed grain structure. Attainment of
equiaxed grains can be regarded as the first step towards this goal and further refinement is devoted to reducing the grain size. This work investigates the approximate minimum dissolved zirconium content necessary for the formation of an equiaxed grain structure in a selected Mg–Zn–Ca alloy. The purpose is to provide a point of reference, both fundamentally and technically, for grain refinement of magnesium alloys with zirconium.

2. Experimental procedure

The approach used to determine the approximate minimum dissolved zirconium content for the formation of equiaxed grains consisted of three steps: (i) to produce samples with the columnar to equiaxed transition (CET) by the addition of zirconium, (ii) to determine the dissolved zirconium contents in the equiaxed grains ahead of the columnar front, and (iii) to verify and amend, if necessary, the zirconium content thus determined by actual grain refining tests. The rationale for the proposed approach will be discussed in Section 4.

The experimental alloy selected had a nominal composition of Mg–3.8%Zn–2.2%Ca, which was based on the chemistry of ZK40 with the addition of 2.2%Ca. The Zn content was purposely controlled below 4% and the Ca content above 2%. This is because zinc in excess of 4% reacts with zirconium to form intermetallics [8]. The addition of 2.2%Ca was due to the considerations that (i) a calcium content of 1% and above could substantially improve the resistance of molten magnesium to oxidation and ignition [9] and (ii) calcium levels above 2% can significantly decrease the castability problems encountered at low levels of calcium, such as cold shuts, hot cracking and die sticking [10].

Melting was conducted in a coated mild steel crucible, protected by 0.4%SF₆ in N₂. A 6 kg batch of the alloy was made by alloying pure zinc at 680 °C and pure calcium at 780 °C to molten magnesium. In actual experiments, the weight of each melt prepared was approximately 1250 g by remelting a slice of the ingot in a coated small stainless steel crucible. Zirconium was introduced to the melt in the form of a Mg–33.3%Zr master alloy at 730 °C. Manual stirring at a rate of about 90 stroke/min was applied following the addition of the master alloy for 2 min to assist the dissolution of zirconium.

Samples examined for the CET were prepared as follows. A mild steel conical mould (dimensions of cavity: Ø36 mm × Ø22 mm × 45 mm; wall thickness: 2.2 mm), preheated at 730 °C in the melting furnace, was dipped into the melt in the crucible and held for 15 min to ensure a uniform temperature of 730 °C. After that, the conical mould was withdrawn from the melt and placed on a refractory brick in the melting furnace. The melt was then allowed to solidify in the closed melting furnace by switching off the power. The cooling rate recorded in the furnace averaged 1.2 °C/min. The conical mould was withdrawn from the furnace at 600 °C. For comparison, samples were also prepared by casting the melt into the same conical mould (at room temperature) from 730 °C, with and without the addition of zirconium.

Samples for metallographic examination were all cut from the cones and polished following standard procedures. An acetic-picral etching solution (10 ml acetic acid, 4.2 g picric acid, 10 ml H₂O and 140 ml ethanol) was used. The microstructures were examined using a Zeiss optical microscope. The zirconium contents in the equiaxed grains ahead of the columnar front were determined by electron probe microanalysis. The dissolved zirconium contents in cast samples were determined approximately using an approach developed previously [11].

3. Results

Fig. 1 shows an overview of the CET observed in a conical sample, where the melt was inoculated with an addition of 1.5%Zr. A transition from columnar to equiaxed grains was observed at about 2–3 mm below the melt surface (Fig. 2). An abrupt change in grain structure was also observed in samples of the base alloy prepared under similar conditions but without the addition of zirconium. Fig. 3(a) provides a glimpse of the transition zone observed in one such sample, where randomly oriented dendrites were observed ahead of the columnar dendrite front. Further away from the columnar front are nearly equiaxed dendrites, Fig. 3(b). The CET shown in Fig. 2 was reproducible with an addition of 1%Zr under similar conditions, but without the addition of zirconium, there is no indication of the formation of equiaxed grains, as shown in Fig. 3(a) and (b). It is clear from these observations that

Fig. 1. The columnar to equiaxed transition observed in a conical sample of the Mg–3.8%Zn–2.2%Ca alloy, where the melt was inoculated with a 1.5%Zr addition in the form of a Mg–33.3%Zr master alloy.
the equiaxed grains shown in Fig. 2 are because of the presence of zirconium.

Fig. 4 summarises the zirconium contents obtained from probing a total of 27 small equiaxed grains just ahead of the columnar front in the sample shown in Fig. 1. Quantitative electron probe microanalysis was used (accuracy: ~0.1%). The Zr contents detected were not uniform, but most measurements were found to fall in the range between 0.2% and 0.3%. It should be pointed out that not all of the zirconium added to the melt has dissolved into the melt. There were undissolved zirconium particles existing in front of the columnar front.

The observations shown in Figs. 2 and 4 point to the suggestion that the presence of more than 0.20% of dissolved zirconium, in conjunction with a certain amount of undissolved zirconium particles, seems sufficient to give rise to equiaxed grains in the experimental alloy if the undercooling experienced by the melt is similar to that experienced ahead of the columnar front. To test this observation, an addition of 0.25%Zr was made to the base alloy at 730 °C. After alloying, the melt was cast into the same conical mould (used at room temperature) and subsequently allowed to solidify in the air. The resulting dissolved zirconium content was 0.22%. Fig. 5(a) and (b) show typical views of the grain structure captured from the edge and the central region, respectively, from the middle height of the sample. Although the resulting grain structure is not uniform, it is free of dendrites and, on the whole, fairly close to equiaxed (the grain structure is dendritic without zirconium). The observations from the
CET experiments are thus reasonably instrumental for the formation of equiaxed grains in the experimental alloy.

4. Discussion

4.1. Rationale for determining the approximate minimum Zr content from a CET experiment

The equiaxed zone ahead of a columnar front can be induced by a number of mechanisms [12]. However, when a grain refiner or an efficient substrate is present, constitutional undercooling driven heterogeneous nucleation is believed to play an important role [12,13]. Zirconium is a potent substrate for magnesium. The CET experiments conducted were designed on the hypothesis that, in the presence of zirconium substrates, heterogeneous nucleation would occur ahead of the columnar front once the undercooling suffices to induce heterogeneous nucleation, depending upon the substrate sizes. A primary consideration in designing the CET experiments was to allow sufficient settling of the zirconium particles to occur in the melt, so that heterogeneous nucleation ahead of the columnar front would only be able to occur on tiny substrates, at an anticipated undercooling comparable to that experienced in sand casting.

The constitutional undercooling arising from the dissolved zirconium ahead of the columnar front can be approximately estimated as follows. According to the new Mg–Zr phase diagram [3,4], the liquidus temperature between the melting point of pure magnesium (650 °C) and the peritectic temperature (653.56 °C, composition: 0.443%) can be approximately described by

$$T_l = \frac{653.56 - 0.443}{0.443 - C_{Zr}}$$

(1)

The dissolved zirconium content in the melt ahead of the columnar front has been determined to be in the range between 0.2% and 0.3%. Taking $C_{Zr} = 0.25$, Eq. (1) gives $T_l = 652.01$ °C. On the other hand, the dissolved zirconium content in the columnar grains at the interface was found to vary between 0.0% and 0.15%. The interface temperature therefore falls in the range between 650 °C and 651.21 °C according to Eq. (1). Since the cooling rate used in this study is very slow (1.2 °C/min), the temperature gradient ahead of the columnar front is reasonably flat. As a result, the melt temperature just ahead of the columnar front can be reasonably assumed to be in the range between 650 °C and 651.21 °C. Accordingly, the resulting constitutional undercooling from the presence of 0.25% dissolved zirconium ahead of the columnar front is in the range between 0.8 °C (652.01 – 651.21) and 2.01 °C (652.01 – 650).

It has been shown that the settling of zirconium particles in a stationary magnesium melt can be reasonably described by [14]

$$S \approx g(\rho_{Zr} - \rho_{Mg})d^2 \frac{18\eta}{t}$$

(2)
where \( S \) is the settling distance, \( g \) is the gravitational acceleration, \( \rho \) is the density (\( \rho_{Zr} = 6.52; \rho_{Mg} = 1.584 \) [15]), \( d \) is the particle size, \( \eta \) is the viscosity of molten magnesium, where \( \eta(T \, ^{\circ}C) = 1.25 \times 10^{-3} - 2.54 \times 10^{-4} (T - 650) \) (N s m\(^{-2}\)) (the equation was extracted from Fig. 1.9 of Ref. [16]), and \( t \) is the settling time. Also, it has been found that the settling of zirconium particles in molten magnesium occurs predominantly within the first 2 h and then reaches a stabilised stage [14]. The melt in the conical mould was subjected to 15 min of settling before cooling started. Together with the cooling time from 730 °C to the liquidus temperature 632 °C (1.2 °C/min), the total settling time was approximately 97 min. Taking the depth of the columnar zone as the settling distance, i.e. \( S = 3 \) mm, Eq. (2) predicts that the 97 min of settling will eliminate any Zr particles larger than 0.49 \( \mu \)m in diameter from the top of the melt. The undercooling (\( \Delta T \)) required to overcome the free-growth barrier for the effective initiation of a grain on such particles can be estimated from \( \Delta T = -2\gamma_{SL}T_m/(\eta \cdot r^*) \) according to the free-growth model proposed for potent substrates [17]. For magnesium, \( T_m = 923 \) K, \( \gamma_{SL} = 115 \times 10^{-3} \) J m\(^{-2}\) [18], and the latent heat of fusion per unit volume of solid magnesium is given by \( L_v = 8.79 \times 1.656/24.305 = 5.989 \times 10^3 \) J m\(^{-3}\) \( (L_m = 8.79 \) kJ mol\(^{-1}\) [19]). Substituting \( r^* = 0.245 \) \( \mu \)m gives \( \Delta T = 1.45 \) K. This is in the range of constitutional undercooling 0.8–2.01 °C estimated previously based on the presence of 0.25% dissolved zirconium.

Actual measurements were made of the thermal undercooling experienced by molten pure magnesium when cast into a similar mild steel conical mould (used at room temperature without preheating) from 730 °C. It was found that the thermal undercooling experienced in the mould was between 0.9 K and 3 K. It is thus not surprising from an undercooling point of view that the dissolved zirconium contents obtained from the CET experiments have been instrumental in inducing equiaxed grains in the conical sample shown in Fig. 5(a) and (b). Many sand-cast magnesium components have a similar solidification environment. As a result, the 0.2–0.3%Zr content is expected to be similarly instrumental under these circumstances.

### 4.2. Optimum grain refinement with zirconium

Apart from the proposed peritectic mechanism, Emley [1] also believed that only zirconium-rich particles that precipitated out from the melt near the peritectic temperature (653.56 °C) were able to act as heterogeneous nuclei for magnesium grains. It is clear from the present study that, under conditions close to sand casting, grain refinement can be achieved at an addition level much lower than the proposed peritectic composition for the binary Mg–Zr system. Generally, this can be attributed to the combined effects of undissolved zirconium particles, as nucleation sites, and dissolved zirconium, as a growth restriction element [20]. Peritectic reaction does not necessarily need to be involved in such cases. As pointed out earlier, the formation of equiaxed grains can be regarded as the first step towards optimum grain refinement. Naturally, starting from the conditions established, further increasing the dissolved zirconium content and the number of nucleating particles in the melt should lead the way to optimum grain refinement. One such example is shown in Fig. 6(a) and (b), where the experimental alloy was inoculated with an addition of 1.5%Zr at 730 °C following the similar procedure and cast into the same conical mould (used at room temperature) under similar conditions. As can be seen, very fine and nearly spherical grains were obtained, where the resulting dissolved zirconium was 0.40% and the undisolved was 1.07%. The addition of 1.5%Zr was made to ensure that the dissolved zirconium could readily reach the predicted solubility level 0.443%Zr. The result obtained (0.40%Zr) tends to support the reassessed solubility level. The addition of zirconium can be reduced with improved alloying efficiency. Currently it is still not possible to predict the minimum level of addition of zirconium required for optimum grain refinement. Assuming the grain refinement achieved in Fig. 6 is close to the optimum, a

![Fig. 6. Very fine and uniform grain structures obtained in a conical sample of the Mg–3.8%Zn–2.2%Ca alloy, cast at 730 °C after grain refinement with an addition of 1.5%Zr. The resulting dissolved zirconium content in the melt was 0.40% (a) was taken from the edge, average grain size (AGS): ~15 \( \mu \)m, and (b) from the central region of the cone, AGS: ~30 \( \mu \)m.](image-url)
comparison of the dissolved zirconium contents in the samples shown in Figs. 5 and 6 seems to suggest that, more than 50% of the dissolved zirconium may be needed to contribute to the generation of the equiaxed grain structure. Further work will focus on establishing the optimum grain refining conditions based on the present work.

5. Summary

Experiments that lead to the columnar to equiaxed transition in a Mg–3.8%Zn–2.2%Ca alloy, induced by the addition of zirconium, on the hypothesis of the constitutional undercooling driven heterogeneous nucleation mechanism, have been designed and conducted. The zirconium contents in the equiaxed grains just ahead of the columnar front were found to generally vary in the range between 0.2% and 0.3%. Without the addition of zirconium, the columnar grains transformed to randomly oriented dendrites and no formation of equiaxed grains was observed. Following these observations, it was shown that nearly equiaxed grains were obtainable at the 0.22%Zr content under conditions similar to sand casting. This provides a useful starting point for establishing the optimum grain refining conditions with zirconium. In addition, the observations presented in this study have also shown that grain refinement by zirconium is achievable at an addition level much lower than the proposed peritectic composition for the binary Mg–Zr system under conditions similar to sand casting.

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