AN ANALYSIS OF THE GRAIN REFINEMENT OF MAGNESIUM BY ZIRCONIUM

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Abstract

A Design of Experiments approach was used to conduct a systematic study of the grain refinement of magnesium by zirconium; variables included the amount of zirconium, the pouring temperature, and the settling time prior to casting. Optical microscopy was used to measure the grain size. TEM was used to identify particles that are likely nucleation sites. The TEM results show that a range of particle sizes are likely substrates and that particles which are likely nucleation sites are faceted. Sample dissolution followed by SEM was used to characterize particle size and morphology while an AccuSizer 770 was used to measure particle size distributions, both in the master alloy and grain refined samples. While less than 2% of the total particles serve as nucleation sites, a comparison of the grain density vs. faceted particle density shows close agreement, suggesting that only faceted particles are likely nucleation sites.

Introduction

Zirconium is well known as an excellent grain refiner for magnesium alloys that do not contain aluminum, since aluminum poisons the grain refining ability of zirconium. [1] However, zirconium is a heavy element with a density almost four times that of magnesium (ρ_{Mg} = 1740 kg/m^3, ρ_{Zr} = 6520 kg/m^3). As a result, the addition of zirconium into molten magnesium results in the loss of zirconium by settling, since during melting zirconium particles settle to the bottom of the crucible and are wasted as sludge. As zirconium is expensive, this represents a significant additional cost as well as wastage of material.

The magnesium rich region of the binary Mg-Zr phase diagram [2] (see Figure 1) shows that grain refinement of magnesium can occur in theory by a peritectic reaction at 654°C, where α-zirconium reacts with liquid and forms an α-magnesium phase. Currently, approximately 1 wt% zirconium is currently added to ensure the peritectic reaction and grain refinement. However, in a systematic study of the grain refinement of magnesium, Saha et al. [3] showed that grain refinement was possible at additions less than the solubility limit of 0.5 wt% zirconium. (Note: All compositions reported in this work are in wt%.)

The goal of this study was to understand the mechanism of grain refinement of magnesium by zirconium and identify the requirements for a more efficient grain refiner. A permanent mold based "hockey puck" experimental setup was used to quantify the grain refinement efficacy of zirconium in pure magnesium [3]. A Design of Experiments (DOE) approach was used to conduct a systematic study of the grain refinement behavior of magnesium by zirconium; variables included temperature, settling time, and amount of zirconium addition prior to casting. Optical microscopy was used to measure grain size. Transmission electron microscopy (TEM) was used to explore and establish the orientation relationship between zirconium particles and the parent

magnesium matrix. Sample dissolution followed by scanning electron microscopy (SEM) was used to characterize particle size and morphology while an AccuSizer 770 was used to measure particle size distributions, both in the master alloy and grain refined samples. The results from the above tasks were used to understand the mechanism of grain refinement of magnesium by zirconium and develop insights for engineering efficient zirconium-based grain refiners for magnesium alloys.
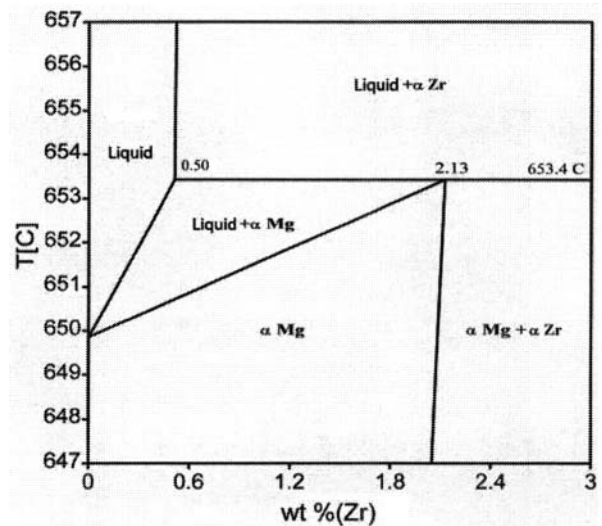

Figure 1. Relevant portion of magnesium-zirconium phase diagram [2] showing peritectic reaction.

Background

Microstructure development in castings is a nucleation and growth process; nucleation is typically heterogeneous. Grain refinement is the introduction of extraneous nucleating agents (grain refiners) to a liquid melt. From classical nucleation theory, the critical radius r^*_{het} for heterogeneous nucleation is calculated as [4]

$$r^*_{het} = -\frac{2\gamma_{SL}}{\Delta G_v} \qquad (1)$$

Where γ_{SL} = solid-liquid interfacial energy, and

ΔG_v = Volume free energy change during solidification (i.e. driving force),

and

$$\Delta G_v = \frac{\Delta H \Delta T}{T_m} \qquad (2)$$

where ΔT is undercooling, defined as the difference between the actual temperature and the equilibrium melting point or liquidus temperature. Undercooling must be negative for solidification to occur.

For magnesium, [5]

T_m = melting point of magnesium = 922.8K,

ΔH = change in enthalpy during solidification
= 5.898 x 10^8 J/m^3, and

γ_{SL} = 115 x 10^{-3} J/m^2.

Then, the critical radius r_{het}^* is given by

$$r_{het}^* = -\frac{0.36}{\Delta T} \quad \text{or} \quad d_{het}^* = -\frac{0.72}{\Delta T} \qquad (3)$$

where d_{het}^* is the diameter or size of the critical radius.

Figure 2 is a plot of Eqn. 3 and shows the undercooling required to nucleate a magnesium grain as a function of zirconium particle size.
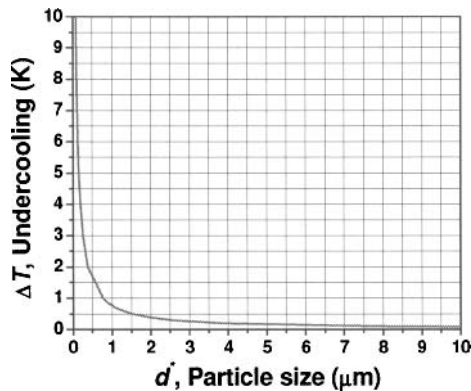

Figure 2. Undercooling required for nucleation of magnesium grain as a function of zirconium particle size.

Nucleation and Growth

Key advances in the understanding of heterogeneous nucleation are due to Turnbull [6] and Sundquist, [7] and of growth to Greer et al. [8] Greer et al. [8] proposed that grain formation is growth limited rather than nucleation limited. They suggested that solidification first occurs on the largest substrates at the lowest undercooling. As undercooling is increased, progressively smaller particles become centers for free growth, which occurs as soon as the required undercooling is reached.

Grain Refinement of Magnesium By Zirconium

Zirconium satisfies all of the requirements of a good grain refiner required by theory, [9] as:

1. Zirconium and magnesium have the same crystal structure (hcp) and the lattice disregistry between them is very small (Zr: a = 0.323 nm, c = 0.514 nm and Mg: a = 0.320 nm, c = 0.520 nm). [10]

2. A peritectic reaction occurs close to 0.5% zirconium at 654°C. A zirconium-rich phase precipitates from the liquid and reacts with magnesium to form an α-magnesium phase.

3. Zirconium has the highest growth restriction factor among all elements that promote grain refinement in magnesium. [10]

While zirconium is an effective grain refiner, it suffers from two drawbacks. First, zirconium is an expensive addition, and excessive zirconium (1%) is added to achieve optimum grain refinement. Second, the zirconium is allowed to settle, as the large

zirconium particles and particle clusters present in the grain refiner master alloy are detrimental to mechanical properties, and this is wasted as sludge.

Qian et al., [11-14] conducted a series of studies on the grain refinement of magnesium. They added 1% zirconium in the form of Zirmax® (Mg-33.3% Zr) master alloy to pure magnesium melt and found undissolved zirconium particles or large clusters (≥ 10 μm). These clusters did not take part in the grain refinement process and settled to the bottom of the crucible. They suggested that only particles between 1 and 5 μm in size acted as nuclei. They also suggested that the majority of grain refinement is achieved from soluble zirconium, although insoluble zirconium particles also contribute to the grain refinement.

DOE Study

Saha et al. [3] conducted experiments with pure magnesium (99.9% Mg) and magnesium-15% zirconium grain refiner master alloy. Three different factors were varied to study grain refinement efficacy – total zirconium addition (0.25, 0.5, and 1%), pouring temperature (705 and 815°C, or 1300 and 1500°F), and settling time (0 and 30 min). A total of 12 experiments were carried out, comprising a full factorial DOE matrix. Figs. 4, 5, and 6 show the variation of the average grain size with total zirconium addition, pouring temperature, and settling time [3].

Doe Study Results

Grain size decreased with increasing zirconium addition for both pouring temperatures and settling times. Also, grain refinement was obtained at 0.25% zirconium, which is less than the solubility limit and less than that required for the peritectic reaction. This shows that zirconium additions less than that needed for the peritectic reaction can produce grain refinement, providing significant new opportunities for increasing zirconium efficiency. A smaller grain size is generally obtained at the higher pouring temperature. Finally, a settling time of 30 min generally resulted in a larger grain size. [3]

TEM Study

TEM analysis was used to identify zirconium particles in grain refined samples that are likely nucleation sites. TEM bright field (BF) microscopy and selected area composite diffraction patterns (SADP) were used to analyze the particle-matrix orientation relationship. For particles which were not electron transparent, high resolution TEM (HRTEM) was used to determine orientation relationships at the particle-matrix interface. The bright field micrographs and diffraction patterns were taken using a Tecnai F-20 TEM operating at 200 keV.

Various particles from a grain refined sample (magnesium-0.5% zirconium, 815°C, 30 min) were observed under TEM. Fig. 3(a) shows a small faceted zirconium particle 0.23 μm in size at the center of a magnesium grain. The SADP of the particle and the matrix illustrated in Fig. 3(b) shows that the particle and the matrix have the same crystallographic orientation. The diffraction spots were indexed based on the [$2\bar{1}\bar{1}0$] direction of the hcp crystal, and all the diffraction spots from the matrix and the particle were exactly superimposed on each other, i.e. the planar disregistry between the low-index planes was very small. The orientation relationship between the particle and the matrix was

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established as $(0001)_{Mg} \parallel (0001)_{Zr}$ and $[2\bar{1}\bar{1}0]_{Mg} \parallel [2\bar{1}\bar{1}0]_{Zr}$, i.e. the basal planes of the particle and matrix had the same orientation. The similarity in the crystal structure and similar lattice spacings between magnesium and zirconium supports the hypothesis that zirconium particles which are likely nucleation sites will show a parallel axis orientation with the matrix.
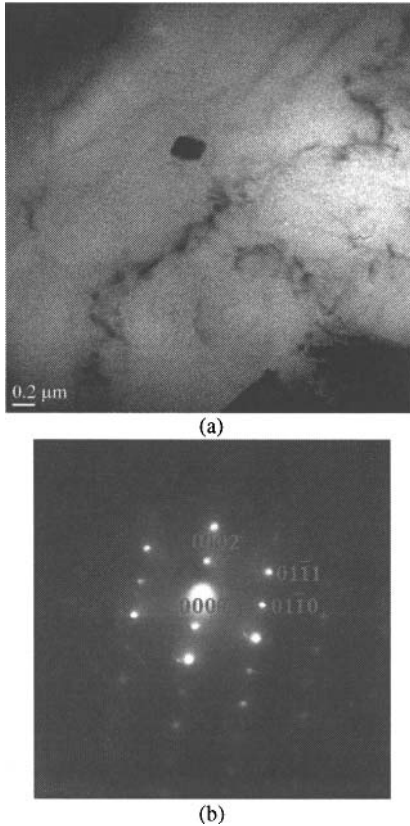

(a)

(b)

Figure 3. (a) TEM bright field micrograph showing a 0.23 μm faceted zirconium particle in the magnesium matrix, and (b) Composite diffraction pattern of particle and matrix showing that diffraction spots are superimposed.

Fig. 4(a) shows a large faceted zirconium particle of 1.6 μm length and 1 μm width) in the matrix at the center of a single grain from the same sample (magnesium-0.5 % zirconium 815°C-30 min grain refined analyzed in Fig. 7. The bright field micrograph suggests that the particle is faceted in nature. The composite selected area diffraction pattern shown in Fig. 4(b) for the particle and matrix reveals that a parallel axis orientation relationship exists between the particle and matrix. The diffraction spots were indexed from the standard $[2\bar{1}\bar{1}0]$ dffraction pattern of an hcp magnesium crystal.

HRTEM was performed at the particle/matrix interface indicated by an arrow in Fig. 4(a). The lattice fringes in Fig. 4(c) are parallel and continuous across the particle-matrix interface and suggest that the particle is coherent with the matrix and there is no atomic misfit or dislocation at the interface. The result suggests that the magnesium grain has grown epitaxially on the zirconium crystal.
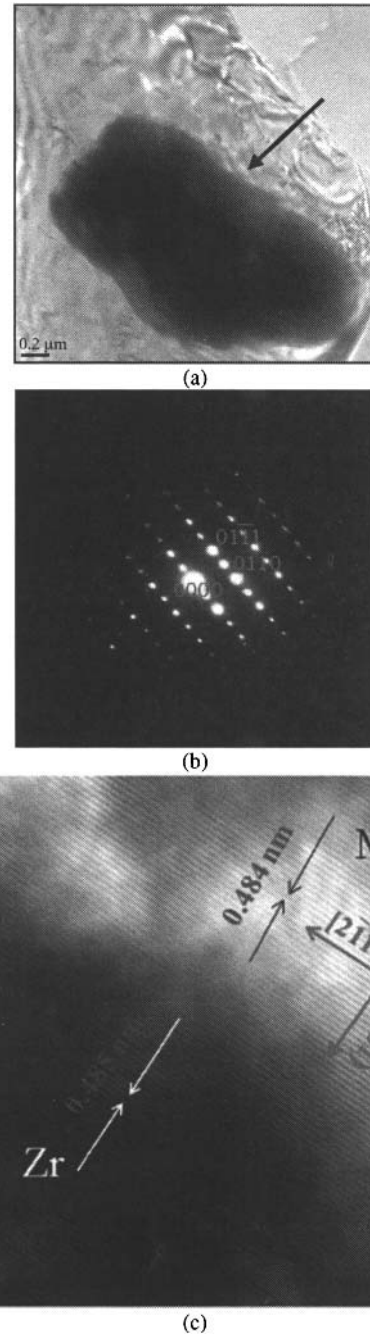

(a)

(b)

(c)

Figure 4. (a) Bright Field TEM micrograph of a zirconium particle (1.6 μm length and 1 μm width) in the matrix, (b) composite diffraction pattern denoting parallel axis orientation of particle and matrix, and (c) HRTEM lattice fringe image at the particle/matrix interface showing parallel and continuous lattice fringes suggesting epitaxial growth of magnesium on zirconium.

Several other particles, both faceted and non-faceted, were found at grain boundaries and did not show any orientation relationship with the matrix, suggesting that they were like not nuclei. This

also suggests that not all particles are selected as nucleation sites and cause grain refinement.

TEM Study: Discussion

The results of this section show that TEM with SADP or HRTEM is an excellent tool for identifying particles that are likely nucleation sites. The TEM study from the magnesium-0.5% zirconium, 815°C pouring temperature, 30 min settling time, grain refined sample showed that a range of zirconium particle sizes (0.23 and 1.6 µm) are likely nucleation sites. (Note: a third particle 0.5 µm in size that showed a parallel axis orientation relationship with the matrix was also found). This supports Greer's free growth theory that nucleating substrates of different size will become active when the required undercooling is achieved. An important observation is that likely nucleation sites, i.e. particles that show parallel axis orientation relationship with small planar disregistry (0.1 to 0.2%) appear to be faceted. This is reasonable as zirconium particles which are faceted in nature are likely to expose a suitable nucleating substrate to the matrix. In particles that exhibited a parallel axis orientation with the matrix, the planes that were parallel were generally either the basal or prismatic planes. HRTEM analysis indicated that in particles that show a parallel axis orientation relationship with the matrix, the lattice fringes at the particle matrix interface are parallel and continuous across the particle-matrix interface and suggest that the particle is coherent with the matrix, suggesting that the magnesium grain has grown epitaxially on the zirconium crystal.

Particle Size and Morphology

The TEM study outlined in the previous section suggested that only faceted particles were likely nucleation sites. In an effort to characterize and quantify particle size, particle size distribution, and particle morphology, samples of zirconium particles were prepared from grain refined samples. Samples were dissolved into 1% diluted hydrochloric acid (0.1 g/10 ml basis) and kept for 72 hrs to digest the sample completely. One ml of the solution was transferred into an EPPENDORF tube and centrifuged at 15000 rpm for 15 min for 3 cycles. After each cycle the liquid was decanted, and de-ionized water was added to the mixture, and the tube was sonicated for 10 min. This allowed magnesium chloride, which is highly soluble in water, to be washed away and for the zirconium particles to be collected at the bottom. Zirconium particle size distributions were determined using an Accusizer model 770 particle size analyzer that uses the light obscuration/photozone method (Particle Technology Labs, Downers Grove, IL, USA).

The final centrifuged sample was ultra-sonicated for 30 min and one drop of the solution was evenly distributed on a silicon wafer. The wafer was dried and kept under vacuum to prevent it from being contaminated. The silicon wafer with the zirconium particles was characterized by SEM at an accelerating voltage of 15 kV, working distance of 10 mm and spot size of 7 nm. Faceted zirconium particles evident from the SEM micrographs were counted using the automated threshold picking tool in NIS-Elements image analysis software. Particles which showed a clear facet and did not have any rounded or curved edges or surfaces were designated as faceted particles. The total number of particles was also counted to determine the percent faceted particles. Faceted particle density was estimated from the particle size distribution data.

Particle Size Distribution

The Accusizer model 770 was only capable of measuring particles greater than 0.5 µm. Also, the particle size analysis data showed that particles greater than 5 µm were present in extremely small numbers. Accordingly, only particle sizes ranging between 0.5 and 5 µm are plotted. Fig. 5 shows the number of particles present in the magnesium-0.25% zirconium grain refined sample at 0 and 30 min. It is observed that the 0 min sample exhibits a wide size distribution and a large number of particles (total count was 83,212 in 1 ml of the dissolution sample) while the 30 min sample has a narrow distribution and a drastically smaller number of particles (total count was 6170 in 1 ml of the dissolution sample). While it might be expected that at 30 min, particles larger than 2 µm particles will settle and be unavailable for grain refinement, the drastic decrease in particles smaller than 2 µm suggests that smaller particles likely coalesced and settled, providing a far smaller particle count at 30 min than expected. The phenomena of particle settling and a consequent increase in grain size is commonly observed in industrial practice and is termed grain refiner fade.

A similar trend was also observed in the magnesium-1% zirconium sample and is shown in Fig. 6. However, the total numbers of particles were relatively high compared to the magnesium-0.25% zirconium sample. This explains why the increase in grain size at 30 min is much smaller at the 1% zirconium level compared to 0.25% zirconium.

Total Particle Efficiency

The fraction of zirconium particles responsible for nucleating grains in each grain refined sample was estimated as the ratio of grain density to particle density. This assumes that each nucleant particle only nucleates a single grain. It was assumed that the total particle density N_v^P (mm^{-3}) was equal to the number of particles present at the start of the melt, i.e. the particle density for the 0 min sample. The grain density N_v^G was calculated as [8]

$$N_v^G = \frac{0.5}{\bar{l}^3}$$

where $\bar{l}$ is the mean lineal intercept of grains.

Table 1 lists the grain size, grain density, particle density, and the nucleant particle efficiency for the magnesium-0.25 and 1% zirconium grain refined samples. It is clear that total particle efficiency decreases with increasing settling time. Importantly, in all cases, the fraction of active zirconium particles is less than 2%, suggesting that only a few of the total particles take part in grain refinement. . Interestingly, Greer et al. [8] in their work on aluminum grain refinement with TIBOR, found that only 1% of TiB$_2$ particles were effective as nuclei.

Faceted Particle Efficiency

Table 2 shows a comparison of the faceted particle density in grain refined samples. It is observed that approximately 2 to 5% of particles present are faceted. Table 3 also shows that the percent of faceted particles increased after 30 min of settling time. The increase in the number of faceted particles at 30 min might be due to the fact that the particles may have dissolved partially and exposed facets in the melt.

Table 3 shows a comparison of the grain density with the faceted particle density. While the total particle efficiency was less than

2% (Table 1), the faceted particle efficiency is around 50% (and varies from 36 to 63%), i.e. a ratio of the grain density to the faceted particle density is approximately half. It is clear that the faceted particle density shows an excellent match with the grain density. This result suggests that only faceted particles are likely active nucleation sites for magnesium grains.

Summary Discussion and Suggestions For Future Grain Refiner Development

Current grain refiners are extremely inefficient; a comparison of grain density with total particle density suggests less than 2% of all particles are active nucleation centers. However, the ratio of the grain density to the faceted particle density is approximately half, suggesting that only faceted particles are active as nucleation centers for magnesium grains. TEM with SADP or HRTEM is an excellent tool for identifying particles in grain refined samples that are likely nucleation sites. Likely nucleation sites are faceted particles that show a parallel axis orientation relationship and small planar disregistry (0.1 to 0.2%) with the matrix. This is reasonable as zirconium particles which are faceted in nature are likely to expose a suitable nucleating site to the matrix. However, only 2 to 5% of all particles are faceted, suggesting that new methods for manufacturing grain refiners need to be developed as the current salt replacement technique is seriously flawed.
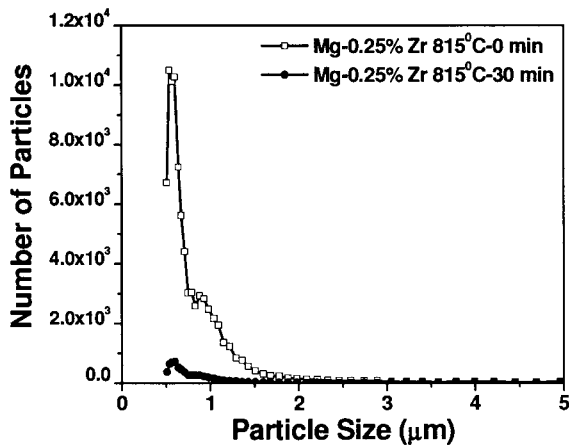
Figure 5. Size distribution of zirconium particles in magnesium-0.25% zirconium grain refined samples at 0 and 30 min. The drastically lower number of particles at 30 min suggests particle agglomeration and settling with time (termed fading).

TEM of grain refined samples showed that a range of zirconium particles act as nucleation sites. This supports Greer's free growth theory that nucleating substrates of various sizes will become active when the required undercooling is achieved, i.e. grain refiners should consist of particles of a range of sizes (e.g. 0.5 to 2 μm).

The dissolution study of grain refined samples suggests that due to the likely coalescence of particles combined with settling, far fewer particles are present at 30 min than would be expected due to settling alone. The reduction in the number of particles at 30 min explains the substantially larger grain size in the 30 min grain refined samples. Thus, the current industrial practice of allowing a melt to settle to allow larger particles to settle out, wastes a lot

more zirconium than previously imagined. A far better approach would be to ensure that the maximum particle size is limited to around 2 μm, to limit any deterioration in mechanical properties, and introduce grain refiners as late as possible (Note: late addition is already current practice in aluminum alloy casting, inoculation of iron, etc. but this work provides quantitative data and further confirms why this is important).

The dissolution study of the grain refined samples also showed that more faceted particles were present in the 30 min sample. It is likely that particles partially dissolved and exposed facet in the melt. This explains why grain size was smaller at the higher pouring temperature, as the higher temperature likely increased the dissolution rate of particles.
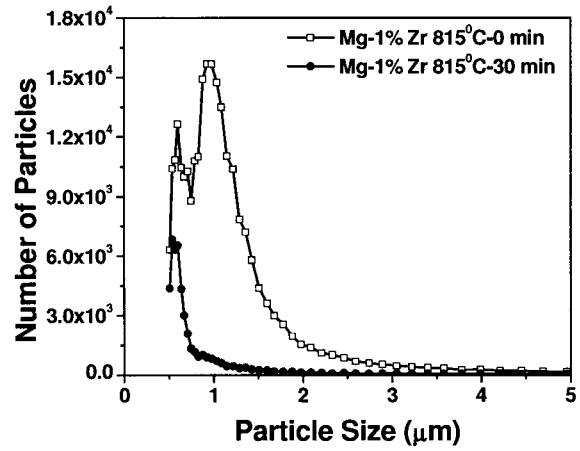
Figure 6. Size distribution of zirconium particles in magnesium-1.0% zirconium grain refined samples at 0 and 30 min.

Table 1. Comparison of nucleant particle efficiency in grain refined samples.

Sample ID	Grain size (μm)	Grain density (mm⁻³)	Total particle density (mm⁻³)	Nucleant particle efficiency (%)
Mg-0.25% Zr 815°C-0 min	109	386	56987	0.68
Mg-0.25% Zr 815°C-30 min	230	41	56987	0.07
Mg-1.0% Zr 815°C-0 min	51	3769	266667	1.41
Mg-1.0% Zr 815°C-30 min	60	2315	266667	0.87

Table 2. Fraction of faceted zirconium particles present in grain refined samples.

Sample ID	No. of total particles	No. of faceted particles	Fraction of faceted particles (%)
Mg-0.25% Zr 815°C- 0 min	599	15	2.5
Mg-0.25% Zr 815°C- 30 min	628	33	5.3
Mg-1.0% Zr 815°C- 0 min	354	8	2.3
Mg-1.0% Zr 815°C- 30 min	348	16	4.6

Table 3. Comparison of faceted particle efficiency in grain refined samples.

Sample ID	Grain size (μm)	Grain density (mm^{-3})	Faceted particle density (mm^{-3})	Faceted particle efficiency (%)
Mg- 0.25% Zr 815°C- 0 min	109	386	952	40.5
Mg- 0.25% Zr 815°C- 30 min	230	41	114	36.0
Mg- 1.0% Zr 815°C- 0 min	51	3769	5973	63.1
Mg- 1.0% Zr 815°C- 30 min	60	2315	6029	38.4

Acknowledgements

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