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ENGINEERING A MORE EFFICIENT ZIRCONIUM GRAIN REFINER FOR MAGNESIUM

S. Viswanathan[1], P. Saha[1], D. Foley[2] and K. T. Hartwig[2]
[1]The University of Alabama, Tuscaloosa, AL 35487
[2]Texas A&M University, College Station, TX 77843

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Abstract

Zirconium is currently used as a grain refiner for high temperature magnesium alloys. However, currently around 1 wt% is used for grain refinement, and much of this is wasted as sludge due to settling, as zirconium has a density almost four times that of magnesium. Since a recent study suggested that only faceted particles were activated as nucleation sites during casting solidification, ECAE processing of a magnesium-15wt% zirconium grain refiner master alloy was attempted to try to increase the number of faceted particles. ECAE processing of the master alloy only resulted in a modest decrease in grain size, even though the percentage of faceted particles doubled as a result of ECAE processing, since only 1.6% of zirconium particles in the as-received master alloy were faceted and deemed to be likely nucleation sites. The results from this work provide insights for the future development of more efficient grain refiners.

Introduction

Grain refinement is an effective method for control of grain size and morphology during casting. The most widespread technique of grain refinement is the introduction of extraneous nucleating agents (grain refiners) to a liquid melt. The benefits from grain refinement include uniform microstructure, distribution of second phase and microporosity on a finer scale, better feeding, and improved mechanical properties. Finer grains also improve surface finish and impart superior machinability. [1] The addition of grain refiners has historically been made as master alloys (often called hardeners) in the form of shot, rod, waffle, or briquette.

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. [2] 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 (see Figure 1) [3] 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. A recent modification [4] of the magnesium-zirconium phase diagram [5] suggests that the maximum solubility of zirconium is 0.5 wt% at 654°C. Currently, approximately 1 wt% zirconium is currently added to ensure grain refinement.

However, in a systematic study of the grain refinement of magnesium, Saha et al. [6] showed that the peritectic reaction was not required for grain refinement. In a further study involving SEM and TEM characterization of grain refined samples, Saha and Viswanathan [7] showed that only faceted particles are likely nucleation sites. Based on these results, this work attempts to reprocess an existing magnesium-15 wt% zirconium master alloy and improve its efficacy, and thereby make it more efficient, i.e. reengineer the grain refiner such that much less than the 1% that is currently used is sufficient for grain refinement.

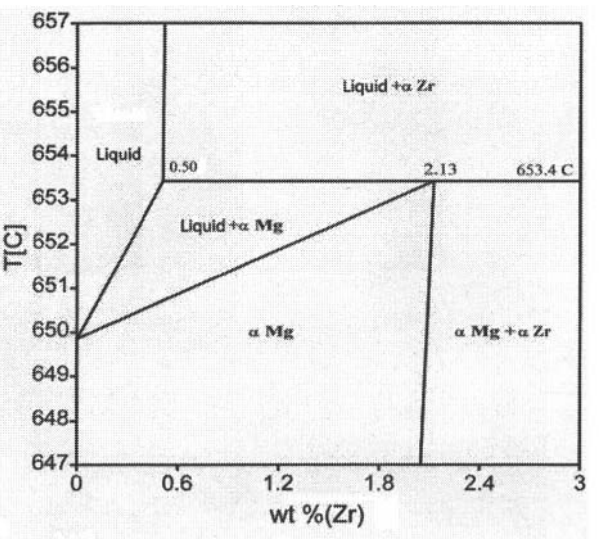


Figure 1. Relevant portion of magnesium-zirconium phase diagram [3] showing peritectic reaction.

Previous Work

Qian et al. [8] found zirconium-rich cores, the majority of which are pure zirconium particles, at the center of magnesium grains or at the grain edge. Electron microprobe analysis of these particles showed that the particle sizes were between 1 and 5 μm, suggesting that only particles within this size range acted as nuclei for the grains. Particles which were greater than 5 μm were not associated with zirconium-rich cores.

Qian et al. [9] also reported on the development of a new magnesium-zirconium master alloy (AM-cast) with zirconium particles smaller than 10 μm. They reported that the newly developed master alloy provided excellent grain refinement when added to pure magnesium. The excellent grain refining ability was attributed to the fine size and even distribution of the zirconium particles in the master alloy. Qian et al. [10] also demonstrated that the efficiency of a Zirmax® master alloy was improved by hot rolling the master alloy ingots into thin plates. The subsequent

improvement in the grain refining behavior was attributed to improved particle size distribution in the rolled master alloy.

Approach

The goal of this program was to increase the grain refinement efficacy of the magnesium-15 wt% zirconium master alloy used in this work, by breaking up large particles and particle clusters and increasing the total number of faceted particles. Accordingly, the master alloy was subjected to severe plastic deformation at an elevated temperature by the Equal Channel Angular Extrusion (ECAE) process. Figure 2 shows an SEM micrograph of the master alloy containing large particles and particle clusters.

Rods 12 mm in diameter and 75 mm in length were machined from the magnesium-15 wt% zirconium master alloy ingot. One rod sample was encapsulated in a steel can (shown in Figure 3) and deformed by ECAE route 4A [11], i.e. 4 passes with no rotation between multiple passes, at 300°C.

The ECAE process spreads out grain boundaries (i.e., elongates the grains as if the material were rolled) and therefore disperses the zirconium particles over a larger volume. [11] For the square billet used in this work, the flow plane is the side plane as the billet exits the ECAE die (see Figure 4). The longitudinal plane is the top of the billet as it exits the die, and the transverse plane is the plane perpendicular to the long axis of the billet. The microstructure in the flow plane of the deformed billet determines how well the ECAE processing has worked for the processing conditions used. For further processing, the ECAE processed billet was sectioned into three pieces as shown in Figure 4. To ensure microstructural uniformity, the center portion was used for all studies. As shown in Figure 4, samples marked 1 and 2 were used for microstructural characterization, and the sample marked 3 was used for dissolution and grain refinement studies.

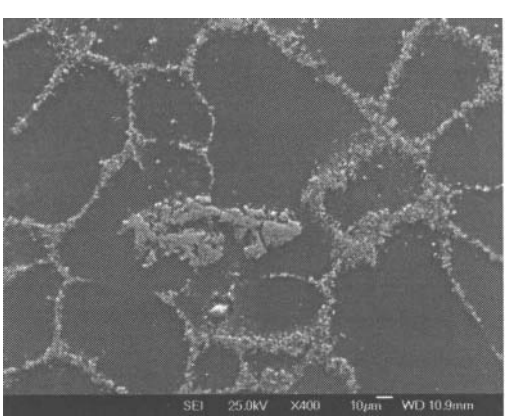


Figure 2. SEM micrograph of the magnesium-15 wt% zirconium master alloy showing large particles and particle clusters.

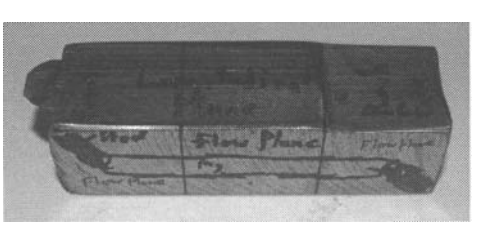


Figure 3. Photograph of magnesium-15 wt% zirconium ECAE processed rod encapsulated in a steel can.

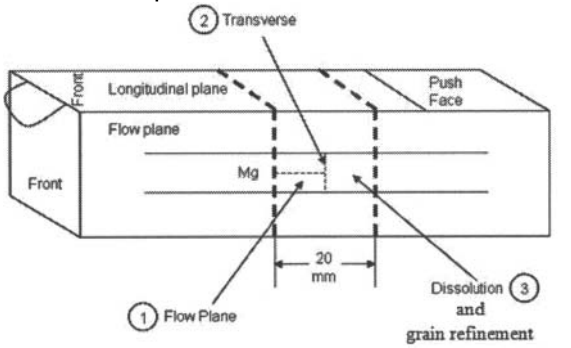


Figure 4. Schematic diagram of the ECAE processed billet showing the flow plane, the longitudinal plane, the push face, and samples (marked 1 to 3) sectioned for microstructural, dissolution, and grain refinement studies.

Characterization of ECAE Billet Microstructure

Figure 5 shows a comparison of the microstructure of the as-received master alloy and the ECAE processed billet. The microstructure of the as-received magnesium-15wt% zirconium master alloy (Figure 5a and Figure 2) contains large zirconium particles along the grain boundary. After ECAE processing, the grains become elongated and the particles are spread along grain boundaries (Figure 5b). The large zirconium particles and particle clusters which were originally at the grain boundary are sheared over a large volume and broken into small individual particles (Figure 5c). Figure 5c was obtained from the boxed region shown in Figure 5b. The micrographs in Figure 5 suggest that ECAE effectively broke up the zirconium particles and particle clusters.

Zirconium Particle Characterization

A sample of zirconium particles was prepared by dissolving the master alloy in acid, which dissolved away the magnesium but did not affect the zirconium. The purpose of the dissolution sample was to determine the particle size distribution, and count the number of faceted particles present in each sample. 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.

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. Figure 6 shows SEM micrographs of zirconium particles from the as-received and ECAE processed master alloy. It is apparent that the zirconium particles in the as-received master alloy are irregular and that some large particles are present (Figure 6a). However, the majority of the particles in the ECAE processed sample appear to

be regular and in the submicron to 2 μm range (Figure 6b). This is likely due to the shearing action of the ECAE process that tends to break up and distribute particles.

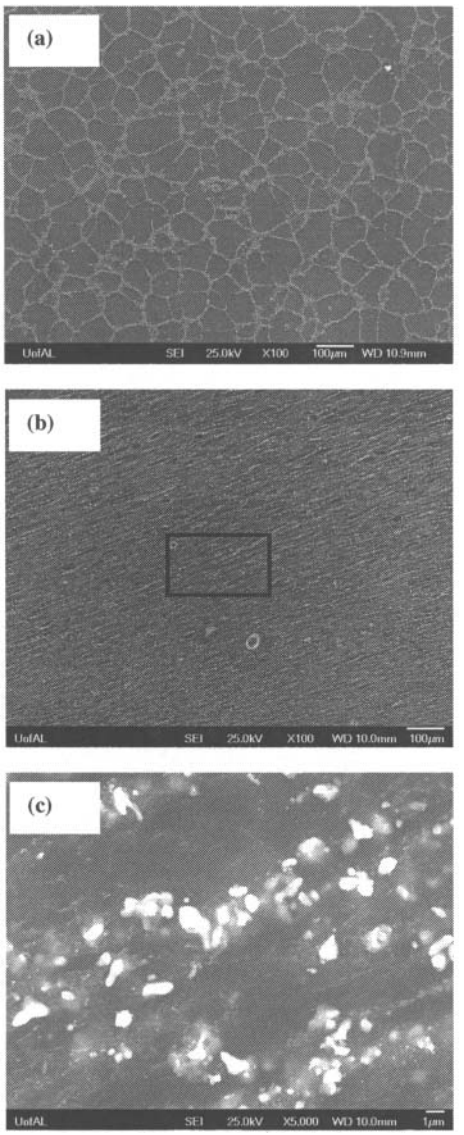


Figure 5. SEM micrographs of (a) as-received Mg-15 wt% Zr master alloy, (b) ECAE processed billet along the flow plane, and (c) enlarged view of a portion of the boxed region in (b) showing breakup and distribution of particles.

The zirconium particle size distributions in the as-received and ECAE processed master alloy samples were determined using an Accusizer model 770 particle size analyzer that uses the light obscuration/photozone method (Particle Technology Labs, Downers Grove, IL, USA). Figure 7 shows the particle size distributions of the as-received and the ECAE processed master alloys. It is apparent that ECAE processing increases the number of particles and narrows the size distribution. It is also apparent that the number of small particles (0.5 to 2 μm) increased in the ECAE processed alloy.

Since Saha and Viswanathan [7] indicated that only faceted particles are likely nucleation sites, the fraction of faceted particles in both the as-received and ECAE processed master alloy samples were estimated from SEM micrographs. Figure 8 shows a typical SEM micrograph showing both faceted and non-faceted particles. Faceted particles were outlined and quantified in terms of area using Nikon NIS-Elements image analysis software. It was found that 1.6% of particles present in the as-received master alloy were faceted, whereas 3.3% of particles in the ECAE processed sample were faceted. The increase in the number of faceted particles suggests that ECAE broke up particles and created more faceted particles.

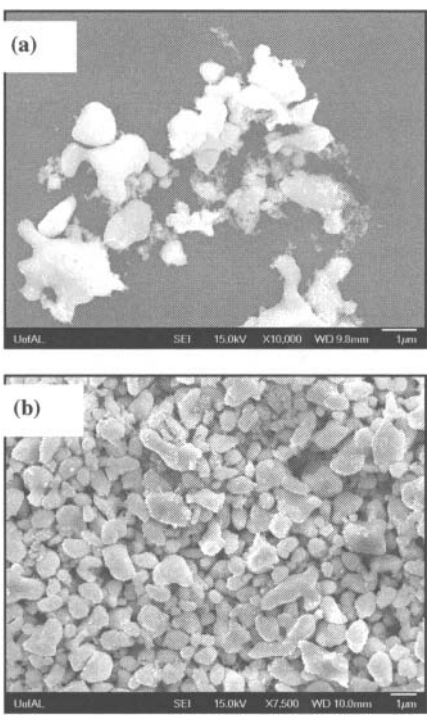


Figure 6. SEM micrographs of zirconium particles obtained from dissolution samples for (a) as-received master alloy, and (b) ECAE processed sample.

Grain Refinement Experiments

Grain refinement experiments were conducted with the original and ECAE processed master alloys. A magnesium-2% zinc alloy was used for the grain refinement experiments. Pure magnesium (99.9%) and zinc were melted in a mild steel crucible using an electrical resistance furnace. The typical melt size was 150 g. A protective gas (0.5% SF6 + CO2) mixture was used to prevent magnesium from burning. Once the desired pouring temperature of 815°C was reached, a small piece of the grain refiner master alloy was added and allowed to dissolve for one minute. The melt was then stirred vigorously for 15 s with a coated mild steel rod and poured into a "hockey puck" mold that was preheated to 350°C. The mold was sectioned from 1018 steel pipe to form a ring mold 45 mm I.D., 63.5 mm O.D., and 12 mm height. A gray iron block, 100 x 100 x 25 mm, was used as the chill. The mold, the chill, and the stirring rod were coated with CONCOTE™

MAG 669 (Hill and Griffith) prior to preheating to 350°C. Figure 9 shows the hockey puck casting setup used for this work.

Metallographic specimens were sectioned from the center of the hockey puck samples using a Buehler Isomet® 1000 precision saw. Specimens were mounted in conductive epoxy using a hot compression mounting process (Buehler Simplimet® 1000). Mounted specimens were ground and polished using standard metallographic techniques. The final polished samples were etched with an acetic picral solution (5 mL acetic acid, 6 g picric acid, 10 mL water and 100 mL ethanol) for 5 s. Optical micrographs were captured with NIS-Elements image analysis software which was integrated with a NIKON EPIPHOT optical microscope. The grain size was calculated at 50x magnification using a standard grain size calculation method. [12, 13]

Since an important goal of this work was to demonstrate that the amount of zirconium could be significantly reduced from the current 1 wt% that is used, 0.1 wt% zirconium (0.67 wt% of master alloy) was added to the magnesium-2% zinc melt and hockey puck samples were poured. Figure 10 shows optical micrographs of the base magnesium-2% zinc alloy without grain refiner addition, and samples grain refined at the 0.1 wt% zirconium level with the as-received and ECAE processed master alloys.

It is clear from the micrographs in Figure 10 that the ECAE processed master alloy had a noticeable improvement on the overall grain refinement compared to the as-received master alloy. This improvement in the grain refinement behavior of the ECAE processed master alloy is attributed to the increased number of faceted particles in the ECAE processed master alloy. However, since ECAE processing only increased faceted particles from 1.6% to 3.3%, the decrease in grain size was modest (Note: particle density correlates with grain density rather than grain size).

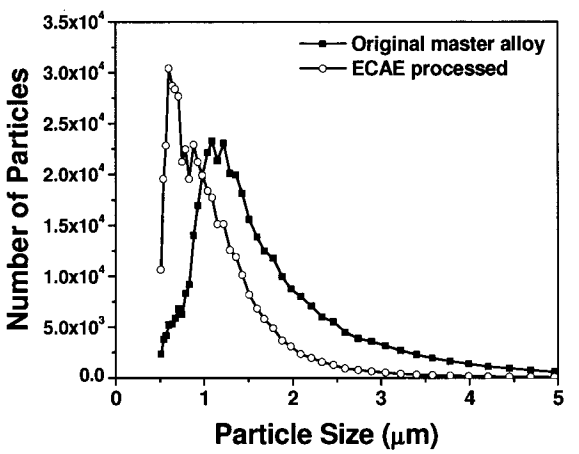


Figure 7. Zirconium particle size distributions in as-received and ECAE processed master alloy samples.

Analysis of Grain Refinement Efficacy

Although the result shown in Figure 10 is encouraging, it is clear that a significant improvement in grain refiner performance will require better up-stream processing of the grain master alloy that results in a higher fraction of faceted particles. To further highlight and explain the link between faceted particles and grain refinement efficacy, faceted particles in the magnesium-2% Zn-0.1% Zr grain refined (hockey puck) samples were also analyzed and counted using the same methodology as that used previously for the master alloys. The results are tabulated in Table 1.

In the data presented in Table 1, each grain is associated with a single nucleus; accordingly, efficiency is the ratio of the grain density to the particle density. Although ECAE processing increased the number of faceted particles, it also resulted in a significantly larger number of particles (i.e. a factor of seven). Accordingly, since there are many more particles, a far smaller percentage of zirconium particles in the ECAE processed master alloy resulted in grains compared to the as-received alloy: 0.17% for the ECAE processed alloy vs. 0.75% for the as-received alloy. However, clearly less than 1% of the zirconium particles in either master alloy are effective, suggesting that current grain refiners are very inefficient. This suggests that the currently used process for making magnesium-zirconium grain refiners, the salt replacement technique in which zirconium salts are reacted with magnesium, needs to be revisited. Interestingly, Greer et al. [14] in their work on aluminum grain refinement with TIBOR, also found that only 1% of TiB_2 particles were effective as nuclei.

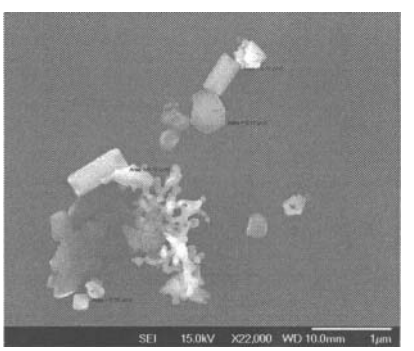


Figure 8. Typical SEM micrograph of zirconium particles obtained from dissolution sample showing both faceted and non-faceted particles. Faceted particles were outlined and quantified in terms of area using image analysis software.

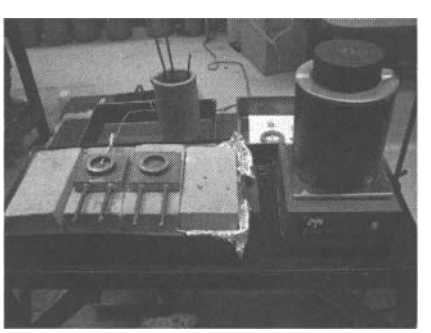
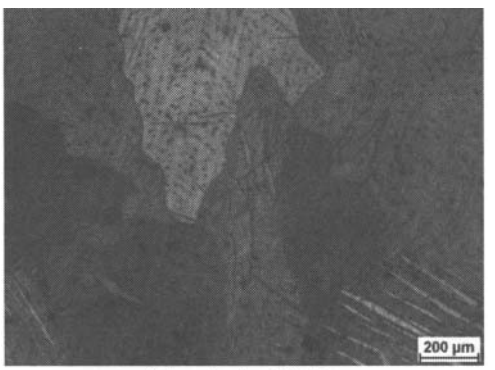


Figure 9. Hockey puck casting setup used for this work.

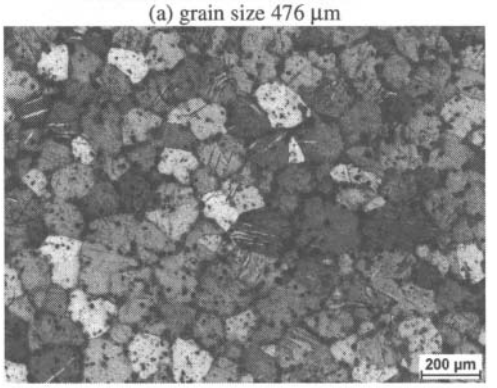
Role of Faceted Particles

The actual increase in the faceted particle density in samples grain refined with the ECAE processed alloy was quite small: 599 vs. 470/mm^3, resulting in only a modest decrease in grain size. (Note:

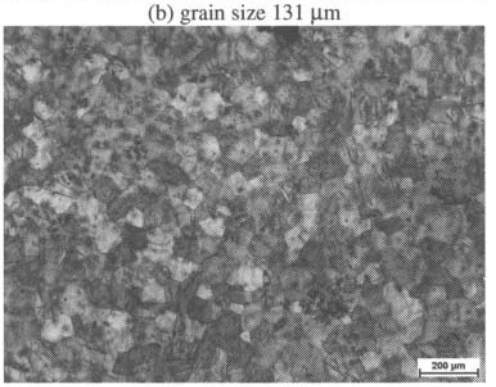
all faceted particles are not selected as nuclei since size is also a factor, as addressed in the next section.) However, the most significant figure in Table 1 is the faceted particle efficiency. While the total efficiency of zirconium particles is less than 1%, the faceted particle efficiency is 50% or higher, i.e. the ratio of grain density to faceted particle density is approximately half. This provides very strong evidence that only faceted particles likely result in grain refinement, i.e. serve as nuclei. These results further corroborate the hypothesis advanced by Saha and Viswanathan [7] that only faceted particles present in grain refiner master alloys are likely active nucleation centers.



(a) grain size 476 µm



(b) grain size 131 µm



(c) grain size 110 µm

Figure 10. Optical micrographs of magnesium-2 wt% zinc samples, a) without grain refiner, b) with 0.1 wt% zirconium using as-received master alloy, and c) with 0.1 wt% zirconium using ECAE processed master alloy. The measured grain size is indicated below the micrographs. (magnification 50x)

Table 1. Analysis of grain refinement efficacy for Mg-2% Zn-0.1% Zr hockey puck samples.

Grain Refiner Used	As-Received	ECAE Processed
Grain size (µm)	131	110
Grain density (mm^{-3})	222	376
Zirconium Particle density (mm^{-3})	29553	214825
Zirconium Particle Efficiency (%)	0.75	0.17
Faceted Particle density (mm^{-3})	470	599
Faceted Particle Efficiency (%)	63	47

Engineering Efficient Grain Refiners

This work provides very strong evidence that grain refiners must be properly engineering to be efficient, and that current grain refiners are extremely inefficient. It is important to note, however, that faceting is not the only factor that determines grain refiner efficacy; another important factor is particle size. The size of the nucleant particle determines the undercooling needed for it to be activated, and the smaller the particle, the larger the undercooling that is required. (Note: the poor efficiency of TIBOR grain refiners is likely related to the size of the particles, since all TiB_2 particles appear to be faceted.) The available undercooling for nucleation is determined by the casting process and the alloy. Moreover, since a range of particle sizes and undercoolings are likely to be active during solidification [14] and measured undercoolings are typically 0 to 2°C, [15] particle size distributions must be also be suitably tailored. Consequently, it is likely that any future effort to develop more efficient grain refiners must target the alloy or alloy family (at least cast vs. wrought) and the process. Finally, the number of suitable particles is also important, as grain density is dependent on nucleant particle density. Therefore, efficient and effective grain refiners must address particle density, particle size, particle size distribution, and particle morphology.

Conclusion

ECAE processing of the magnesium-15 wt% zirconium grain refiner master alloy used for this work provided only a modest improvement in grain refiner efficacy. This is due to the fact that only faceted zirconium particles appear to nucleate grains during solidification. Although ECAE processing doubled the number of faceted particles, the fact that only 1.6% of the particles in the as-received master alloy were faceted limited the extent of improvement that was possible by ECAE processing. This work suggests that future development of efficient and effective grain refiners must address particle density, particle size, particle size distribution, and particle morphology.

Acknowledgments

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