

Grain Refinement of Magnesium Alloys: A Review of Recent Research, Theoretical Developments, and Their Application

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This paper builds on the “Grain Refinement of Mg Alloys” published in 2005 and reviews the grain refinement research on Mg alloys that has been undertaken since then with an emphasis on the theoretical and analytical methods that have been developed. Consideration of recent research results and current theoretical knowledge has highlighted two important factors that affect an alloy’s as-cast grain size. The first factor applies to commercial Mg-Al alloys where it is concluded that impurity and minor elements such as Fe and Mn have a substantially negative impact on grain size because, in combination with Al, intermetallic phases can be formed that tend to poison the more potent native or deliberately added nucleant particles present in the melt. This factor appears to explain the contradictory experimental outcomes reported in the literature and suggests that the search for a more potent and reliable grain refining technology may need to take a different approach. The second factor applies to all alloys and is related to the role of constitutional supercooling which, on the one hand, promotes grain nucleation and, on the other hand, forms a nucleation-free zone preventing further nucleation within this zone, consequently limiting the grain refinement achievable, particularly in low solute-containing alloys. Strategies to reduce the negative impact of these two factors are discussed. Further, the Interdependence model has been shown to apply to a broad range of casting methods from slow cooling gravity die casting to fast cooling high pressure die casting and dynamic methods such as ultrasonic treatment.

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I. INTRODUCTION

THIS paper covers developments since our 2005 Metallurgical and Materials Transactions publication on the Grain Refinement of Magnesium Alloys.^[1] The 2005 paper was in two parts: Firstly, a review of the literature on the grain refinement of magnesium alloys and then the application of our early theoretical work on the grain refinement of aluminum alloys to magnesium alloys. A key conclusion from that paper was that “research needs to focus on gaining a better understanding of the detailed mechanisms by which refinement occurs and gathering data to improve the ability to predict grain refinement for particular combinations of alloy and impurity chemistry and nucleant particles.” Although only a few years have elapsed since making

this statement, an updated review paper is warranted. Since 2005, we have developed the Interdependence Theory^[2] which provides new perspectives for the study of grain refinement. It is a more rigorous model for analyzing grain refinement mechanisms and predicting grain size outcomes. This paper discusses the new theory as it applies to magnesium alloys and reviews several other developments on the grain refinement of magnesium alloys since 2005.

Nucleation of the primary phase is the first step in the transformation of molten alloys into the solid state. As this transformation sets the as-cast grain size of the microstructure, control of nucleation has been the subject of much research.^[1] In the case of magnesium alloys, a finer grain size improves most mechanical properties including yield strength due to the high Hall–Petch coefficient,^[3–6] creep resistance,^[7] and corrosion resistance.^[8–10] In particular, from a strengthening perspective, plastic deformation of hexagonal close-packed (hcp) magnesium begins by activation of the soft basal slip system, followed by prismatic and other hard slip systems as the internal stresses increase. Basal slip leads to the formation of dislocation pileups at grain boundaries and the second phase particles. The ensuing activation of prismatic slip results in linear strain hardening due to the athermal accumulation of dislocations.^[6,11] This differs from the deformation and strengthening of most cubic metals such as Al which show parabolic strengthening. This linear strengthening characteristic offers a useful mechanism for further strengthening. It has been shown that grain refinement can effectively extend the linear

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strengthening process of magnesium alloys.^[6] The strengthening effect or the strong Hall–Petch relationship occurs not only at room temperature, but also holds at relatively high temperatures, *e.g.*, up to 523 K (250 °C) or $0.57T_m$ for Mg–Nd–Zn–Zr alloys.^[12] The technology of grain refinement is thus an important method for obtaining the desired service performance of cast magnesium components over a broad temperature range. A fine initial grain size is also beneficial for further post-casting processes such as extrusion and rolling where it insures a finer uniform grain size after secondary recrystallization.^[13–15]

The status of commercial grain refining methods has not significantly changed since our earlier publication.^[1] That is, Zr refining of alloys that do not contain aluminum is still the best, although an expensive approach to obtaining a fine grain size, while there is still no satisfactory commercial refiner available for Mg–Al-based alloys. However, our understanding of the mechanisms of refinement has advanced providing new insights into the possible strategies that could be used to develop an effective grain refining technology.

After an update of the literature regarding the broader research on grain refinement of magnesium alloys and an introduction to the Interdependence Theory, we revisit the grain refinement of Mg–Al and Mg–Zr-based alloys. Consideration is also given to solidification in dynamic environments such as high pressure die casting and ultrasonic treatment, both of which exhibit a relationship between grain size and alloy chemistry as defined by the growth restriction factor, Q . Finally, we discuss the implications of the theory for future research.

II. REVIEW OF RECENT RESEARCH ON THE GRAIN REFINEMENT OF MAGNESIUM ALLOYS

There have been two main theoretical advances that have taken place over this time. The first is the development of grain refinement models with improved basis in physics. The work of the current authors has shown the importance of solute on the grain refinement process. While this was based on earlier work^[1,16] which presented a simple methodology for evaluating the relative effects of particle potency, density, and solute on the grain size, it has been developed into a physically based model now called the “Interdependence Theory.”^[2,17] This approach has provided insights into the mechanism of grain refinement such as showing that superheating and impurity removal (native grain refinement) have equivalent effects on producing a refined grain size^[18] and that the key difference between Mg–Zr master alloys in terms of their effectiveness is the number of particles of a few microns in size.^[19,20] The Free Growth Theory,^[21] which is another important approach to modeling grain refinement, incorporates a similar role for solute,^[22,23] but it focuses on particle size effects and cooling rate. This model, or developments arising from it, has been used by a number of authors investigating the grain refinement of Mg-based alloys.^[24–26] Two key impacts of these models are that it

is now less common for authors to make judgements about the effectiveness of a nucleant particle on grain refinement based on additions to pure elements and also that the role of solute elements on grain refinement is being actively studied.^[27] The essentials of these theories are presented in Section III.

The other major theoretical advance has been the use of crystallography as an aid to predict potential nucleant particles.^[28–30] Lattice matching has been long recognized as an important factor for a successful nucleant particle.^[31,32] However, the ability to better predict orientation relationships rather than just comparing the lattice registry of close-packed planes is now recognized as a superior analytical method. One of these methods known as edge to edge matching (*e2em*) has enabled researchers to provide a number of insights or hypotheses about the mechanism behind issues such as superheating^[33] and which particles are likely to be better grain refiners.^[30,34–36] It has also led authors to try particular particles that may not have been identified otherwise. While a number of particles have been trialed for Mg–Al alloys and have been found to be somewhat effective, often other factors such as solubility and phase transformations have restricted the identification of an effective grain refiner being found. However, a new nucleant particle has been identified for some rare earth-containing alloys, which will be described in Section II-E.

While Zr continues to be the most effective grain refiner in many Al-free systems, grain refinement of Mg–Al alloys is still a major issue. The next part of this review focuses on grain refinement of Al-containing alloys. It is becoming apparent that despite the range of processes that have been used to grain refine Mg–Al alloys, there are only two major considerations: the effect of minor and impurity elements and the type of nucleating substrates in the melt, particularly now that the role of solute elements is better understood. We do not intend to revisit the information provided in our previous review paper,^[1] but will attempt to link progress to the headings used in that publication.

A. *The Role of Minor/Impurity Elements—The Superheating Effect, the Elfinal Process, and Native Grain Refinement*

It is becoming evident that minor and impurity elements have a major effect on the grain refinement of Mg–Al alloys. Three previously described grain refining approaches, *i.e.*, superheating, the Elfinal process, and native grain refinement, only work in Mg–Al alloys and now appear to be products of this impurity effect. The superheating effect^[37] involves heating the melt to a temperature well above the liquidus of the alloy (often in the range of 180 K to 300 K above the liquidus temperature) for a short time, followed by rapid cooling to, and short holding at, the pouring temperature leading to significant grain refinement. Native grain refinement is the observation that high purity Mg–Al alloys have an inherently finer grain size compared with commercial purity alloys. It should be noted that this is unusual behavior and it is not observed

in Mg-Zn or Mg-Ca alloys^[38] or other alloy systems.^[39] The Elfinal process is the addition of FeCl₃ to Mg-Al melts, where it is assumed that Fe-particles or Fe-containing intermetallics are the nuclei. A discussion on these mechanisms was carried out previously^[1] and detailed analyses can be found in other work.^[38,40] What all of these processes indicate is that minor or impurity elements can have a large effect on the grain size. It has also been noted that the superheating effect and native grain refinement have equivalent effects on the grain size response of Mg-Al alloys, suggesting that the same mechanism is operating in both processes.^[18]

Fe additions reduce the grain size,^[40] including in Al-free alloys.^[41] Cao *et al.*^[40] demonstrated that Fe is a grain refiner for high purity Mg-Al alloys (Fe <10 ppm, Mn <10 ppm) when added in the form of FeCl₃ (the Elfinal process) due to the formation of Al- and Fe-rich intermetallic particles. They^[42] also observed the presence of Al-Fe-C-O compounds and suggested a “temperature-solubility” theory for grain refinement in which superheating controls grain refinement by increasing the number of small particles rather than by changing particle potency. The possibility of Fe-particles or intermetallics acting as nuclei has not been established conclusively. Another possibility is that Fe has a very high relative growth restriction factor, $m(k - 1)$, where m is the liquidus gradient and k the partition coefficient, indicating that its growth restriction effect is very high, although it is limited by its low solubility. It needs to be noted, however, that Fe is a notoriously detrimental element to the corrosion resistance of magnesium alloys.^[43,44]

Mn is usually added to magnesium alloys to remove Fe and improve the corrosion resistance. Many Al-Mn-Fe intermetallics form at a temperature above the liquidus and in particular Al₈(Mn,Fe)₅ formation is used to remove Fe from the alloy.^[45] Some of the phases that can form have been identified as possible grain refiners.^[28,33] An *e2em* crystallographic study by Qiu *et al.*^[33] has shown this is quite possible with the metastable τ Al-Mn(Fe) phase emerging as the preferred candidate rather than the ϵ Al-Mn(Fe), Al₈Mn₅, β -Mn, or others. This phase originates from the transformation of the high temperature ϵ phase on rapid cooling. Zhang *et al.*^[28] had already demonstrated that Al₈(Mn,Fe)₅ is a potential nucleant on crystallographic grounds, but is likely to be much less efficient than either Al₄C₃ or Al₂CO (see Section II-B).

Cao *et al.*^[46] found that Mn additions can be a significant grain refiner, although it depends upon the addition method. It was concluded that the high temperature ϵ -AlMn phase is a preferred nucleant over the lower temperature Al₈Mn₅ phase as the grain refining ability was lost on longer holding times. This should be compared with the proposed superheating mechanism in which the τ Al-Mn(Fe) phase arising from the transformation of the high temperature ϵ phase may be the most crystallographically favorable substrate for Mg nucleation.^[33] Others have claimed that the grain size of AZ91 can be reduced by using Al₈(Mn,Fe)₅ particles as effective nucleants for magnesium grains,^[47-50] although not everyone agrees that this is effective.^[51]

It appears that Al₈Mn₅ is a possible nucleant for α -Mg, although if more potent nuclei are added to Mg-Al alloys, it is likely that the Al₈Mn₅ may nucleate on such particles, hence the discussion about the role of duplex particles by some authors.^[48,52,53] If potent nuclei are added, their effectiveness may be limited by the presence of phases that precipitate prior to α -Mg which may coat the potent nuclei with the less effective nucleant, Al₈Mn₅. This may explain that while the beneficial grain refining effect of Mn has been observed by others,^[54] it is also noted that in the presence of carbon-based grain refining additions, Mn does not improve grain refinement and may even have a negative effect.^[54-56]

This analysis means that an early hypothesis for the superheating effect, namely that Al-Fe or Al-Mn-Fe intermetallic phases precipitate from the melt on cooling and subsequently act as nucleation sites for magnesium grains,^[57] has now been modified. It is suggested that the actual mechanism is the thermal reinvigoration of the native grain refining particles due to the dissolution of the poisoning phases formed by Fe and Mn impurities combined with Al.^[58] The loss of grain refinement on holding at a reduced temperature prior to casting is thus proposed to be due to gradual reprecipitation of the poisoning phase over the surface of the native particles. This modified theory appears to reasonably explain the similarity in the grain refining response of superheating and native nucleants.

Other explanations that have been proposed include the formation of Al₄C₃ particles due to an uptake of carbon from the steel crucible^[57] accounting for the presence of native refining particles, although this appears to be incorrect as refinement due to superheating still occurs when high purity materials are made in inert melting vessels.^[58] Also, nucleation on magnesium oxides, aluminum oxides, or similar non-metallic inclusions that may form during the superheating process has been proposed,^[59,60] although the explanation seems to be less likely than the one proposed above as it cannot explain native nucleation. Therefore, understanding the effect of minor and impurity elements is critical to understanding grain refinement in Mg-Al alloys.

B. Carbon-Based Grain Refiners

Similar to superheating, carbon inoculation (in its various forms) is effective only in magnesium alloys that contain aluminum.^[61-65] Mg-Al type alloys that can be effectively grain refined by carbon inoculation normally contain more than 2 pct Al.^[62-64,66,67] The main issues continue to be the form the carbon should be in when added to the melt and identifying the actual mechanism of grain refinement.

C₂Cl₆ (hexachloroethane) is known to be an effective grain refining addition and work continues on this method.^[61,68-70] However, there are significant toxicity concerns related to its use. A number of researchers have investigated alternatives to C₂Cl₆ including the use of carbon-containing master alloys^[52,53,71] and charcoal.^[72]

C has also been added^[73] (in various possible forms) together with niobium pentoxide or vanadium pentoxide

(at 0.1 to 0.3 pct levels as powder or in pelletised form) and later MnO₂ at ~0.2 pct^[74-76] as alternative carbon carriers. Compared with adding carbon without a carrier, enhanced grain refinement (<100 μm) was obtained in AZ alloys.

Another effective approach to adding carbon, which may be less harmful than C₂Cl₆, is the use of carbonates, particularly MgCO₃^[77] and MnCO₃,^[50] although it may be the oxide-based as much as the C-based particles that enhance grain refinement. Direct carbon addition *via* a pulsating argon gas stream was reported by Yano *et al.*^[78] HFC (hydrofluorocarbon) compounds have also been investigated with a moderate grain refining effect being identified.^[79]

Although SiC was proposed early on as a nucleant for Mg alloys, it has recently been the focus of renewed research activity.^[5,24,26,55,80] Papakyriacou *et al.* describe the manufacture and use of SiC in an Al-infiltrated preform as a grain refiner for Mg-Al alloys.^[81] Easton *et al.*^[55] have used this SiC master alloy and shown effective grain refinement across a range of Al contents. However, EDX analysis found Mg₂Si to be present, giving indirect evidence of SiC reacting with molten Mg. Liu *et al.*,^[56] with their master alloy of SiC particles in an Al matrix, also produced good grain refinement in AZ31 and AZ63 alloys, but not in AZ91.

The mechanism of carbon inoculation has been a subject of debate. Carbon segregation has been postulated as a theory,^[68] although is unlikely on the grounds of insufficient C solubility (<20 ppm), the ineffectiveness of C in Al-free Mg alloys,^[62] and the eutectic regions being depleted of carbon.^[48,82] More likely is the formation of an effective carbon-based nucleant particle.

Al₄C₃ particles are effective nucleants for magnesium grains as originally proposed by Emley.^[57] This has been demonstrated thermodynamically and crystallographically by Lu *et al.*^[83] and later experimentally by the addition of 1 pct of 3 μm Al₄C₃ particles to high purity Mg-3Al alloy (low Fe, Mn) prepared in an inert crucible.^[84] However, SiC particles have been found to be more effective than Al₄C₃ at least by some authors,^[85] even though they may not be stable in the melt.^[55]

Oxygen (O) has been found associated with Al and C in particles at grain centers in Mg-Al alloys inoculated with C.^[66,86] Jin *et al.*^[68] argued for nucleation on Al-C-O particles (rather than Al₄C₃) based on lattice matching, and *e2em* has also demonstrated crystallographically that Al₂CO is potentially a better grain refiner than Al₄C₃.^[28] However, it is more probable that Al₄C₃ is the nucleant and that the Al-C-O compounds observed in microstructures are the result of aqueous sample preparation techniques,^[62,84] given the extremely low free oxygen content in molten magnesium.

Most recently, some clarity has been obtained regarding the nucleant particle composition formed on the addition of SiC.^[87,88] Instead of being either SiC or Al₄C₃, Al₂MgC₂ was observed and its planar disregistry with α-Mg is less than that of Al₄C₃. This satisfies the many observations described above related to Mg₂Si formation with the addition of SiC, the importance of Al being present as well as the effectiveness of C inoculation. It has also been claimed that Al₄C₃ and Al₂MgC₂ can be simultaneously present as nuclei.^[72]

Carbon inoculation has been used by the magnesium industry for decades now. It works, but a more effective approach suited to commercial production, particularly to direct chill casting of magnesium ingot, billet, or slab materials, has long been desired.

C. Deliberate Addition of Alloying Elements and Inoculants to Promote Grain Refinement

The deliberate addition of particular inoculant particles is a common approach to grain refining. In Mg-Al alloys, many compounds have been tried, but so far none has been adopted by the industry. Alloying additions have also been investigated and these may form compounds that act as nuclei or increase the growth restriction effect of the alloy. Our 2005 review^[1] included Sr, rare earths (RE), Th, Si, Ca, B, AlN, MgO, TiB₂, and TiC.^[89-91] Some of these and other additions are discussed below.

1. Strontium/calcium

Small additions of Sr were found to be effective as a grain refiner for pure magnesium or low Al content magnesium alloys (*e.g.*, 1 pct Al), but not for high Al content alloys.^[89,92] However, others^[93,94] have claimed that Sr additions can refine high Al content Mg-Al alloys as well. Sr has a reasonable growth restriction effect, which may be the reason for the benefit.^[1] Addition methods may lead to variations in the grain refining response.^[95,96] Y additions along with Sr have been found to be beneficial for grain size reduction.^[97] Calcium additions have also been found to be effective and have been associated with the formation of Al₂Ca^[98] in addition to the growth restricting effect of Ca which is particularly important in lean alloys such as AZ31.

2. Borides

Titanium diboride particles are used to grain refine aluminum alloys. They also have good lattice matching with Mg^[30] and are, therefore, good candidates for grain refining Mg-Al alloys. TiB₂ particles or master alloys containing TiB₂ particles have been added to Mg-Al alloys and show effective grain refinement,^[90,99-101] although the required level of addition varies. ZrB₂ particles have also been found effective,^[102] but fade, due to particle settling, is a problem. The use of boron additions of at least 0.0005 pct has also been claimed to be effective in the presence of Mn^[103] and a substantial amount of trace Zr or Ti.^[104] Interestingly, Ti alone has also been found to grain refine Mg-Al alloys, with the optimum addition ranging from 0.03 to 0.1 wt pct Ti before an increase in grain size is observed.^[105,106]

3. Other particle and alloying additions

Boron Nitride was proposed as a grain refiner for Mg alloys containing Al, Ti, Zr, and/or Th by Bach *et al.*^[107] A recent Chinese patent^[108] claims that an alloy of Mg-Al-Zn-Mn with La melted together under vacuum or argon leads to <40 μm grain size in cast bars. A recent patent application^[106] for Ti addition lists the following other possible materials in the prior art: particles such as

Table I. A Summary of the Approaches Taken to Grain Refine Mg-Al Alloys With the Positives and Negatives of Each Approach

Process	Positives	Negatives
Solute additions	can lead to significant grain size reduction even without the addition of a nucleant	there is a limit to the grain refinement that can be achieved and it is not effective in casting alloys which already have high solute contents
Superheating	significant grain refinement can be achieved	very difficult to control. High temperatures [−1123 K (850 °C)] must be used that can cause melt handling problems. Not clear what the nucleant particles are the only approach used commercially at this stage; however, the most effective way of adding C is still up for debate
C inoculation	significant grain refinement can be achieved	grain refinement is not as effective as desired. SiC is unstable in the melt and appears to be another C-inoculation technique
SiC	reasonably effective	results vary suggesting that the reason for the grain refinement cannot be controlled. It is not understood completely why they work
Fe, Mn, Ti additions	reported that some grain refinement achieved. However, poisoning occurs when Fe and Mn are both present	borides have been tried and have been found to show inconsistent results
Borides	these are known nucleants in Al-based alloys and are available as master alloys. Reports of good grain refinement	ZnO is unstable in melts and a previous attempt at using AlN particles did not perform as well as expected. More work is required
AlN, ZnO	<i>e2em</i> predictions suggest these are possible nucleants	

Al₄C₃, AlN, SiC, TiC, and CaC₂ and/or solute elements such as B, C, Ce, La, Nd, Sr, and Y. Ce in combination with either Sr or Ca has also been shown to lead to moderate grain refinement in AZ91.^[109]

Lee *et al.*^[92] studied several nucleant particles, TiC, AlN, SiC, and Al₄C₃, claiming that the latter two had the strongest grain refining effect. Although AlN seems to have been proposed on the basis that it may be associated with formation of Al₄C₃ when C is added (as per reports in the 1950s), it has since been demonstrated to have a good crystallographic match in its own right using the *e2em* model.^[35] Kretz *et al.*^[85] noted in a crystallographic table that both AlN and ZnO might be potential nucleant substrates, but they did not pursue these. These compounds have also been identified using *e2em*.^[36] However, ZnO has been shown to be rapidly reduced by Mg to Zn solute.^[36] Nevertheless, the grain refinement achieved by the ZnO additions was still greater than that gained by an equivalent addition of Zn solute. This suggests that ZnO may actually be useful in short-contact time grain refining situations. Al₂O₃ has also been found to be an effective grain refiner.^[5]

D. Summary of Mg-Al Refinement Observations

In summary, a suitable grain refiner for Mg-Al alloys is still elusive and none of the approaches discussed has been satisfactory in a commercial sense. A summary of the types of grain refinement methods and a brief critique of each are given in Table I.

The three general directions of resolving the grain refinement problem in Mg-Al alloys are therefore (1) to find a new additive that will perform the task, (2) to significantly improve the efficiency of an existing process, or (3) to use a non-chemical approach. The first two options require a much better understanding of what controls the formation and/or poisoning of nucleant particles in Mg-Al alloys, while the third option will be discussed in Section II-F.

E. Grain Refinement of Rare Earth (RE)-Containing Alloys

Mg-Zr addition is almost the perfect grain refiner except that it is not able to grain refine Al-containing alloys due to the affinity of Al for Zr reacting to form Al₃Zr. Limited research has been undertaken to understand why Zr is such a remarkably effective grain refiner. Perhaps this is due to an assumption that improvements cannot be made to these master alloys beyond their current performance. Zr-based grain refiners will be discussed in more detail in Section III-B.

A new development in recent grain refinement research is that Al in combination with some of the rare earths can provide very effective grain refinement and may be an option to replace Zr additions in these alloys. The *e2em* model predicts that Al₂Y particles should be good nucleant particles and Al additions to Mg-Y alloys showed that this is indeed the case.^[34,110] The grain refining effectiveness is almost as good as Zr, with the further benefit of a much lower tendency to grain coarsening during heat treatment. Similar effects have been found in Mg-Gd alloys.^[111] The

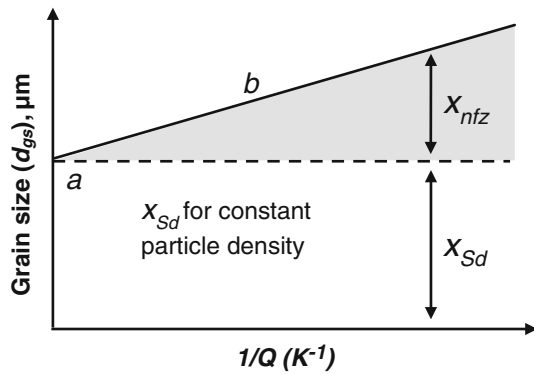


Fig. 2—A simple representation illustrating that for each value of Q , the grain size is the result of the two components described by Eq. [2] where x_{Sd} is the average distance to the activated particles and b is equal to the gradient of x_{nfz} over a unit of $1/Q$. The shaded area is the nucleation-free zone (nfz) and the difference between values of b and a represents the minimum grain size that can be achieved for each value of Q at very high particle density (*i.e.*, when a tends to zero). It is assumed that the particle number density is constant and, therefore, $a = x_{Sd}$. Adapted from Ref. [2].

where D is the diffusion coefficient, v is the rate of growth of the solid–liquid (S–L) interface, C_1^* is the composition of the liquid at the S–L interface at x_{cs} , ΔT_{n-min} is the undercooling required for nucleation on the largest available particle, and $z\Delta T_{n-min}$ is the incremental amount of undercooling required to activate the next nucleation event as the temperature gradient moves toward the thermal center of the casting. The constant 4.6 is a cut-off factor for the solute profile in front of the S–L interface where $(C_l(x') - C_o)/(C_1^* - C_o) = 1$ pct.^[2]

The three terms in Eq. [1] are (1) x_{cs} , the distance which a previously nucleated grain must grow in order to establish sufficient CS ahead of the solid–liquid (S–L) interface to enable nucleation of the next grain on the nearest most potent particle (*i.e.*, where CS equals or exceeds the nucleation undercooling for this particle, ΔT_{n-min})^[17]; (2) x'_{dl} , the diffusion distance from this S–L interface to the point where the critical amount of CS has been generated; and (3) x_{Sd} , the additional distance to the location of the most potent available nucleant particle that actually nucleates the new grain.

Figure 2 shows the relationship between these three terms over a range of Q values calculated from the alloy composition. The first two terms are determined from the alloy characteristics and the casting conditions defining the formation of the CS zone, and together are referred to as the nucleation-free zone (x_{nfz}) as insufficient CS is developed within this zone to cause a nucleation event to occur.^[2] The third term x_{Sd} is defined by the distance to where the CS zone intersects the particle size/potency distribution $\Delta T_n - S_d$. The value of x_{Sd} is decreased by increasing the particle number density by, for example, adding more Zr master alloy.

It should be noted that the main part of the second term, $\frac{C_1^* - C_o}{C_1^* \cdot (1-k)}$, can be converted to $\frac{\Delta T_n}{Q}$ as $\Delta T_n = m(C_o - C_1^*)$ which is inserted into the numerator and $Q = mC_o(k - 1)$ which can be inserted into the

denominator when ΔT_n is small and, therefore, C_1^* is close to C_o . These substitutions into Eq. [1] for an incremental increase in undercooling, $z\Delta T_{n-min}$, give

$$d_{gs} = 5.6 \left(\frac{D \cdot z\Delta T_n}{v \cdot Q} \right) + x_{Sd} \quad [2]$$

Equation [2] highlights the two key factors, the first term which is equal to x_{nfz} and x_{Sd} , that together determine the grain size^[20].

By plotting the grain size data in the form illustrated by Figure 2, the Interdependence model can provide information on the relative potency of naturally occurring and deliberately added nucleant particles (related to b in Figure 2 and equal to the first term in Eq. [2]) as well as the maximum number of active nucleant particles (related to a in Figure 2 and equal to the second term, x_{Sd} , in Eq. [2] for a constant particle number density).^[2,16-18,132,133]

Figure 2 also represents the basis for using Eq. [2] to predict grain size. The value of the intercept with the y-axis, a , is related to the maximum particle number density of particles that are able to be activated as nucleation sites for the formation of new grains. This value is difficult to predict and in many cases, there is no information about the particle distribution and in the case of Mg–Al alloys, we do not know with any certainty what the type and composition of the particles are (see Section II). Therefore, this value is assumed to be the intercept derived by experimentally determining the grain size for a range of alloy compositions converted to their Q values. We can attempt to predict the slope of line b by using data from the literature for the parameters in the first term or matching the slope by manipulating these values if they are not available in the literature.^[2] These two approaches are illustrated in the following sections to provide insight into some of the key unresolved problems in the grain refinement of Mg alloys.

A. Grain Refinement of Mg–Al Alloys

Based on our analysis^[18] of grain size data versus $1/Q$ for commercial and high purity Mg–Al alloys,^[38] Figure 3 reveals that the slope of the line of best fit is significantly different for commercial and high purity alloys. Given that the casting conditions are the same and the intercepts on Figure 3 are similar (*i.e.*, the particle number densities are similar), the only cause of this difference is the potency of the active nucleant particles. The nucleation undercoolings from experiment (Table II) support this finding. Clearly, the chemistry difference between commercial and high purity alloys is the cause of this change with the main difference being the presence of Fe and Mn. As Al is an important factor in causing poisoning,^[1] it is likely that an AlMnFe-type layer is formed on the native nucleants. It is still not clear what the native nucleants might be: oxide particles, Al_4C_3 , or other mixed carbides, or other compounds containing Mn, Fe, N, and/or O (see Section II-A).

Similar experiments were carried out on superheating and it was observed that when commercial alloys were

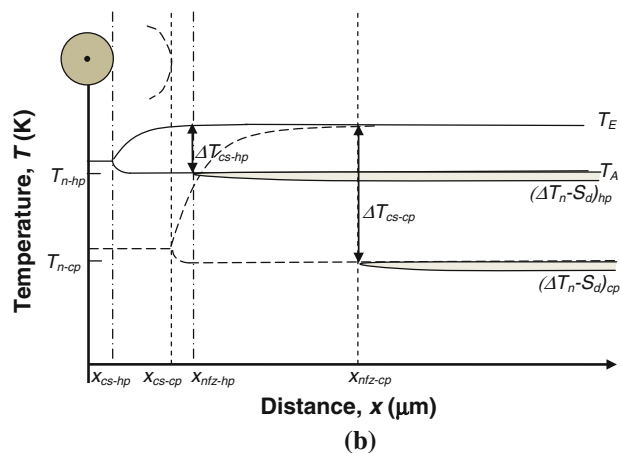
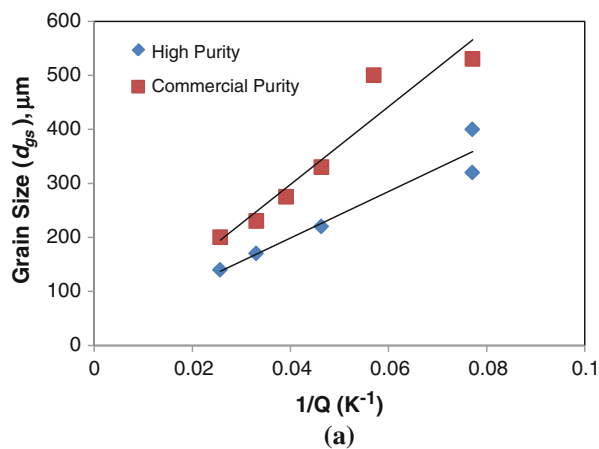


Fig. 3—(a) Grain size versus $1/Q$ for a range of commercial purity and high purity Mg-Al alloys from 3 to 9 wt pct Al (after Ref. [18]). A plot of grain size predicted by Eq. [1] is equivalent to the lines of best fit. (b) Representation of two narrow particle distributions, $(\Delta T_n - S_d)_{cp}$ and $(\Delta T_n - S_d)_{hp}$, of different potencies (shaded) resulting in a very small or negligible value of the interparticle spacing, x_{sd} . Note: these particle distributions are very different from that shown in Figure 1.

Table II. Values of D and v , m , and k from the Mg-Al Phase Diagram and the Composition Ranges of C_o Investigated in the Analysis by the Interdependence Theory

Diffusion Coefficient, D [$m^2 s^{-1}$]	5×10^{-9}
Growth velocity, v [ms^{-1}]	2×10^{-6}
Liquidus slope, m [K/wt pct]	-6.87
Partition coefficient, k	0.37
Nucleation undercooling, ΔT_n [K]	2.2 (high purity) 5.5 (commercial purity)
Range of C_o [wt pct]	<11.0 (Al)

superheated, the obtained grain sizes coincided with those measured for the high purity alloys.^[18] This observation strongly implies that the mechanism is the same where the intermetallic layer which poisons refinement in commercial alloys is dissolved during superheating. This mechanism suggests that mechanical methods such as melt conditioning (see Section II-F) may be successful through fracturing the particles and/or surface layers and consequent exposure of the native particles beneath the poisoning layer.

While Fe and Mn added separately produce a degree of refinement, it is clear from the above that small amounts of Fe and Mn present together can have a significant negative effect on the grain refinement of Mg-Al alloys. This also implies that research aimed at introducing alternative nucleant particles of potentially higher potency can be affected by Fe and Mn present in commercial alloys. Successful experiments on the addition of alternative nucleant particles may be due to higher purity base alloys, a change in the Fe:Mn ratio to a ratio where poisoning does not occur, or holding times after refiner addition that are too short for the formation of the impurity layer. However, the underlying risk is that these particles will not be effective in a range of commercial alloys and casting processes. Pertinent issues include narrow phase composition limits leading to phase instability, casting conditions which form metastable phases, and Fe/C pickup from crucibles—all of which make for an unstable grain refining system. These factors could explain much of the confusion in the literature arising from contradictory findings related to the grain refinement of Mg-Al alloys.

The Interdependence equation, Eq. [1], enables the prediction of grain size based on parametric data drawn from the literature (Table III).^[2] The correspondence between the experimentally determined slope and the predicted slope is very good.

By using the conceptual framework of the Interdependence Theory, Figure 3(b) schematically shows the location of the high and commercial purity particle distributions relative to the formation of the CS zone and that the particle potency distributions must be narrow. It also reveals that the nucleation-free zone is the dominant factor controlling grain size. Despite the fact that there are a very large number of particles as indicated by the very low value of the intercept in Figure 3(a), most of the particles do not result in the nucleation of grains.

For the commercial alloys studied, it is apparent from Figure 3(a) that the only approach to reducing grain size is to reduce the size of the nucleation-free zone, x_{nfz} . Of the parameters that determine the value of x_{nfz} in Eq. [2], it might be possible to reduce ΔT_n (i.e., increase the potency) by modifying the chemistry of the impurity layer; increase Q by increasing the Al content or by adding ternary elements with a high growth restriction coefficient; increase v by increasing the cooling rate; or decrease the diffusion rate D through alloying. Of these options, changing ΔT_n and/or v may be feasible approaches. For example, the effect of increasing cooling rate and thus v was observed in studies on high pressure die cast alloys (Table III). Alternatively, ultrasonic treatment (Section II-F) or melt conditioning may decrease the average ΔT_n , providing significant additional refinement.

The effect of casting conditions on the refinement of Mg-Al alloys is well illustrated through comparison with the microstructures produced by high pressure die casting (HPDC). The grain size distribution in HPDC alloys tends to be bimodal^[4,134] with coarse externally solidified grains (ESGs) formed in the shot sleeve being swept into the casting during the latter stages of die

Table III. Comparison Between Experimentally Determined Values of the Gradient of Grain Size Versus $1/Q$ and Those Predicted by Eq. [1] Using the Input Data Presented in this Table

Alloy system	Gradient b measured (predicted)	Input data
Mg-Al alloys		
High purity	4307 (4291)	$D = 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $z\Delta T_n = 0.31 \text{ K}$, $v = 2 \times 10^{-6} \text{ m s}^{-1}$
Commercial purity	7217 (7274)	$D = 5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $z\Delta T_n = 0.53 \text{ K}$, $v = 2 \times 10^{-6} \text{ m s}^{-1}$
Ultrasonic	490	
High pressure die cast	17.9	
Mg-Zr alloys	1418 (after accounting for increasing particle number density)	$D = 3.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, $z\Delta T_n = 0.015 \text{ K}$, $v = 2.1 \times 10^{-7} \text{ m s}^{-1}$

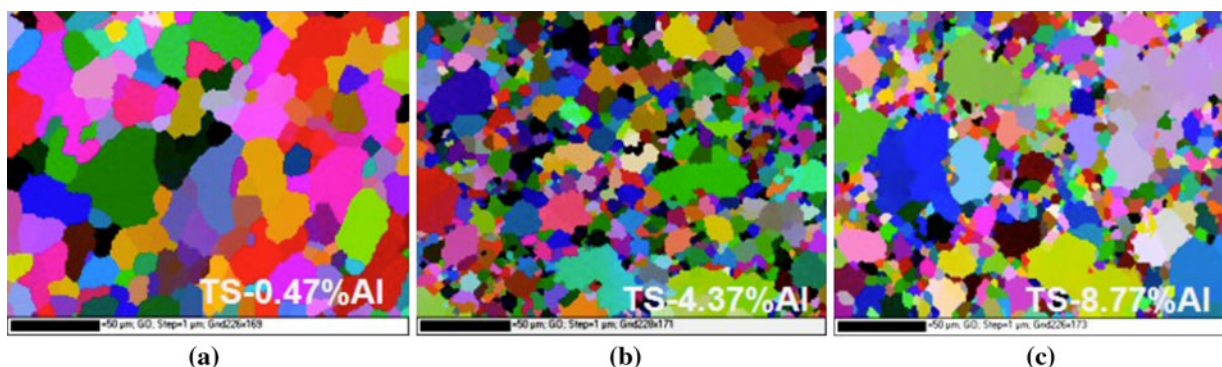


Fig. 4—Images obtained from electron backscattered diffraction patterns where different colors indicate different grain orientations.^[135] The images are from near the top surface of the HPDC castings for (a) Mg-0.47Al, (b) Mg-4.37Al, and (c) Mg-8.77Al alloys.

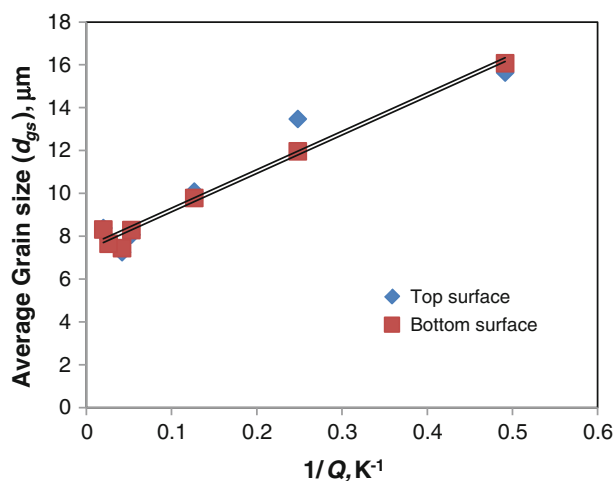


Fig. 5—The median grain size of Mg-Al high pressure die cast alloys near the top and bottom surfaces for a range of Al contents plotted against $1/Q$.^[135] Rectangular cross-section specimens were used.

filling. While these coarse grains are the most problematic aspect of grain size control in HPDC, it is interesting that the Al content affects the finer grain size formed in the die cavity during HPDC^[135] just as it does in casting operations with slower cooling rates. In Figure 4, the grain sizes near the edge of some HPDC Mg-Al alloys are shown and a linear relationship is observed between grain size and $1/Q$ (Figure 5). Hence, even with very rapid cooling rates, a similar mechanism of grain refinement is operating.

The fitting equation through the data in Figure 5 is $d_{gs} = 7.5 + 17.9/Q$. The very low value of the slope b is indicative of the very high cooling rate in high pressure die casting. This corresponds to very high values of v in Eqs. [1] and [2].

B. Grain Refinement of Mg-Zr-based Alloys

The excellent performance of Zr in Al-free alloys is due to good crystallographic matching between Zr and Mg and the high growth restriction of dissolved Zr. The maximum solubility of Zr in molten Mg is about 0.45 pct, while the total addition of Zr is typically in the range of 1 to 3 pct.^[136] Hence, not all of the added Zr particles completely dissolve and both potent Zr particles and solute Zr are present in commercial practice.^[137,138] Once the solubility limit has been achieved in the Mg melt, further addition of Zr only increases the number of particles.

There are a few types of Mg-Zr master alloys available and all are based on Zr particles and particle clusters within a matrix of Mg.^[19,139] The Mg matrix readily melts on addition to molten alloys, but stirring is needed to dissolve sufficient Zr to provide the necessary growth restriction.^[138] Despite the similarity in the behavior of the master alloys, they produce different levels of grain refinement and waste Zr due to settling.^[19] Figure 6(a) shows the size distribution of Zr particles for three master alloys and (b) the plots of grain size versus $1/Q$ obtained for each master alloy. It has been observed that particles of a few microns in

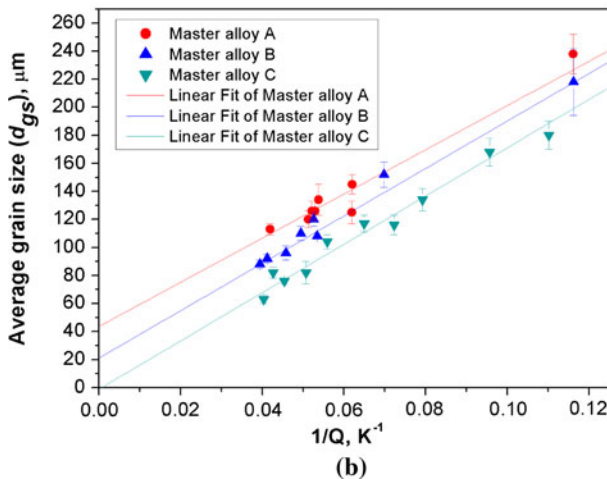
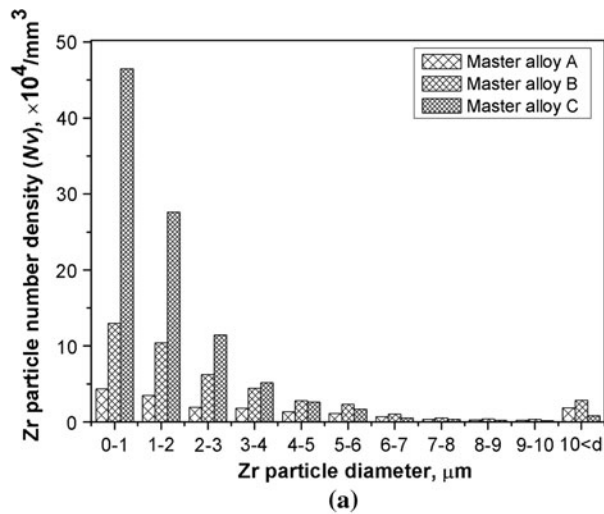


Fig. 6—(a) The distribution of all the Zr particles in 1 μm diameter intervals for three Mg-Zr master alloy defined by N_v , number density ($\text{No.}/\text{mm}^3$). Master alloy A is a commercially available Chinese master alloy, Mg-30 pct Zr alloy; master alloy B is Zirmax[®], a Mg-33 pct Zr alloy; and master alloy C is AM-CAST[®],^[139] a Mg-25 pct Zr alloy. (b) Grain size d_{gs} vs $1/Q$ for a range of Mg-Gd-Y-Zr alloys after the addition of the three Mg-Zr master alloys. Data from Ref. [20].

diameter are found in the center of grains,^[20,123] while particles greater than 5 μm settle to the bottom of the crucible during the holding time after stirring.^[20,140] When melt is withdrawn from the top of the crucible for casting, the particle size distribution will be similar to that of the master alloy shown in Figure 6(a), but only for the particles below 5 μm . Taking this into consideration, it can be readily seen that master alloy C has many more particles in this size range than master alloys B and A. Figure 6(b) shows that the as-cast grain size matches this trend with master alloy C producing the finest grain size and master alloy A the largest grain size.

Because Zr simultaneously provides both solute and potent particles, there is a complication in applying the Interdependence Theory to Mg-Zr-based alloys. To be able to use the theory, the increase in particle number density with increasing Zr content needs to be taken into account. Figure 7 schematically illustrates the effect of increasing particle number density with increasing Q .

A modification^[20] to the second term in Eq. [2] can be tailored to the Mg-Zr system as follows:

$$d_{gs} = 5.6 \left(\frac{D \cdot z \Delta T_n}{v \cdot Q} \right) + \frac{1000}{\sqrt[3]{\frac{Zr_A}{Zr_{MA}} \cdot N_v(d_{pi} \leq d_p \leq d_{pj})}} \quad [3]$$

where Zr_A is the amount of Zr added, Zr_{MA} is the weight percent of Zr in the master alloy, and N_v is number density of Zr particles that are able to become active and which are defined by the size range between d_{pi} and d_{pj} (in μm).

It was found that all of the largest particle sizes (*i.e.*, 1 to 5 μm) present in a casting are able to nucleate a grain. The average undercooling measured corresponding to the first major nucleation events was about 0.15 K,^[141] indicative of the high potency of these Zr particles. Detailed microscopic observations suggest that some undissolved Zr particles (irregularly shaped) also nucleate magnesium grains.^[142] Once the increase in particle number density with increasing Q is taken into account (Figure 7), the slope b (as shown in Figure 2) which is due only to the nucleation-free zone was calculated.^[20] This slope provides an indication of the potency of the Zr particles. A value of about 1418 for the slope is significantly less than the slopes determined for the Mg-Al alloys (Table III), confirming the good grain refining performance obtained from Zr additions.

Using Eq. [3] to predict grain size requires an estimate to be made of most of the parameters in the first term as values for D and v are not available in the literature. ΔT_n is actually an average value of the range of particle sizes that participate in nucleation.^[20] Sensitivity analysis shows that relatively small changes to some of these parameters can make a large difference to the prediction outcome. However, a process of matching the predicted slope of the grain size vs $1/Q$ plots to the experimentally determined slopes can provide an indication of what these values might be. Further significant research is required to improve the accuracy of these predictions.

As was found for the Mg-Al alloys, the nucleation-free zone has a significant effect on the grain size and the efficiency of the master alloy. For the alloys produced in a recent study,^[20] it was found that only 2 to 3 pct of the Zr particles from the master alloy are activated as nucleation sites for the formation of new grains. Unlike TiB_2 particles in molten aluminum, the fast settling of Zr particles from a master alloy addition may have contributed to the inefficiency.^[140] However, despite this inefficiency, very fine grain sizes can be achieved in commercial casting environments.

Equation [3] indicates that further improvement can be obtained by reducing the values of either or both x_{nfz} and x_{sd} . Regarding x_{nfz} , a reduction in ΔT_n can have a significant impact. Given that a range of particle sizes is able to nucleate a grain, the best approach would be to increase the number density of particles with the largest useful sizes, thus reducing the average value of ΔT_n . If this is achievable, then x_{sd} will also be decreased. One method to do this is simply to select a master alloy with the highest particle number density such as master alloy C. Another approach is to apply a mechanical approach

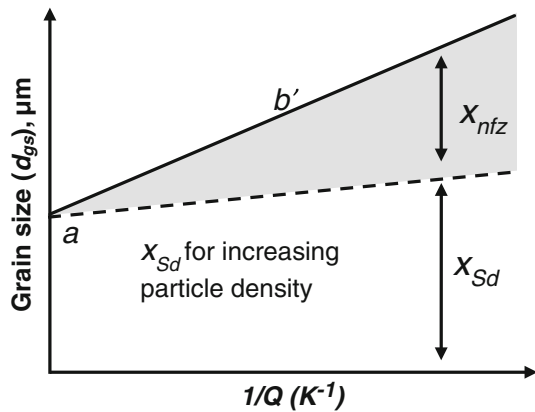


Fig. 7—Figure 2 is adapted to take into account an increasing particle number density as Q increases. b' is the slope of x_{nfz} plus the slope of x_{Sd} corresponding to increasing the particle number density with Q (i.e., x_{Sd} decreases as Q increases).

such as melt conditioning that will disperse the Zr particle clusters.^[126]

Commercial practice is based on the use of reliable Mg-Zr master alloy grain refiners. It should be noted that most commercially important Zr-containing Mg alloys are sand cast Mg-RE-based alloys used predominantly in the T6 state, and the T6 grain size could be different from the as-cast grain size due to grain growth.^[12]

C. Grain Refinement of Mg-Al Alloys via Ultrasonic Treatment

The positive effects of dynamic conditions on the solidification of metals have been recognized for many years.^[143,144] Ultrasonic treatment (commonly termed “ultrasonication”), in particular, is one simple means that has been shown to be effective for various alloys^[143,145,146] and was demonstrated on large aluminum alloy ingots.^[143] Acoustic cavitation is essential to ultrasonic grain refinement.^[143] Accordingly, the ultrasonic amplitude applied needs to exceed a certain cavitation threshold that depends on alloy chemistry. Figure 8(a) shows the influence of the ultrasonic intensity, measured by the square of the ultrasonic amplitude (A), on grain refinement of Mg-Al alloys.^[143] The cavitation threshold varied from $A = 1 \mu\text{m}$ for the Mg-8 pct Al alloy to approximately $A = 6.5 \mu\text{m}$ for the other three alloys (Mg-3 pct Al, Mg-1 pct Al, and Mg-0.5 pct Al). Figure 8(b) replots the grain size data in Figure 8(a) vs $1/Q$ for $A \geq 6.5 \mu\text{m}$.

The slopes of the lines of best fit corresponding to $A = 15, 20, 25 \mu\text{m}$ in Figure 8(b) are essentially the same, while the intercept decreases. These observations reveal that increasing the ultrasonic amplitude above the threshold refines the grain structure mainly by activating more nucleant particles, but the potency of the particles is little changed. On the other hand, the noticeable change in the slope of the line of best fit from $A = 6.5 \mu\text{m}$ to $A = 15 \mu\text{m}$ signifies the transition from underdeveloped cavitation to developed cavitation, and thus Figure 8(b) can be used to help determine the cavitation threshold.

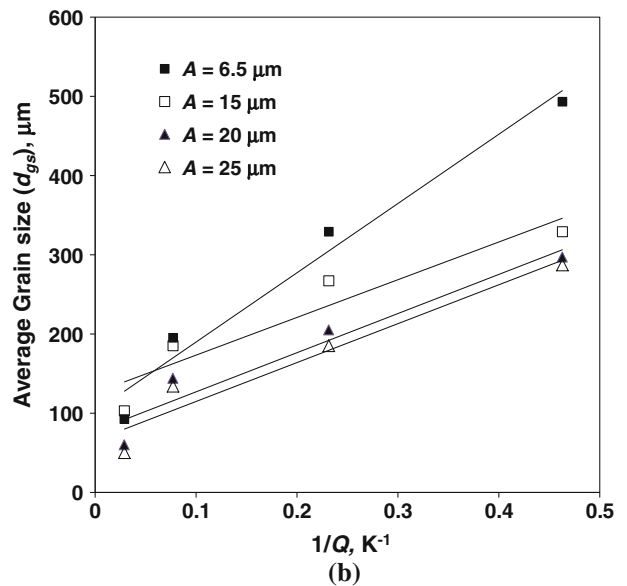
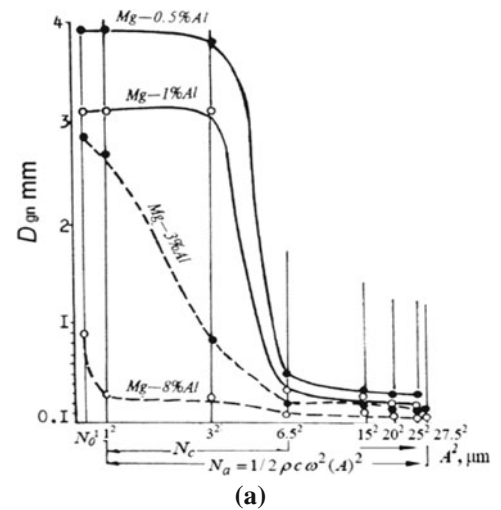


Fig. 8—(a) Refinement of the structure of Mg-Al alloys vs ultrasonic intensity, where A is the ultrasound amplitude (μm). Reproduced from Ref. [143]. (b) Grain size data replotted vs $1/Q$ for the four Mg-Al alloy compositions shown in (a) with respect to different ultrasonic intensities measured by the square of the ultrasound amplitude (A).

Recent work on ultrasonic refinement of binary Mg-Al and Mg-Zn alloys^[142,147] and commercial magnesium alloys^[146,148,149] has further confirmed that the inverse growth restriction model applies to microstructural refinement by intensive ultrasonication.

If we restrict this analysis to amplitudes above the cavitation threshold, then Eq. [2] can be modified to

$$d_{gs} = 5.6 \left(\frac{D \cdot z \Delta T_n}{v \cdot Q} \right) + \frac{1}{\sqrt[3]{f(A) N_v}} \quad [4]$$

where A is the ultrasound amplitude. For a given cooling rate, ultrasonic grain refinement thus depends primarily on the amplitude of the ultrasonic waves and the solute composition of the alloy. A recent detailed experimental study of the ultrasonic grain refinement of binary and

commercial Mg alloys resulted in the following findings^[147]: (1) ultrasonication leads to significant grain refinement only in the presence of adequate solute, which is alloy dependent; (2) the attendant grain number density increases linearly with increasing solute content at a given ultrasonic amplitude; (3) increasing the solute content above the cavitation threshold is more effective than substantially increasing the ultrasonication amplitude; and (4) the difference in grain size between two ultrasonicated magnesium alloys is mainly determined by the solute content rather than the irradiation amplitude. If the resultant grain size is plotted vs $1/Q$, it always shows a near perfect linear relationship for both binary and commercial grade magnesium alloys.^[146,148–150] On the other hand, it can be assumed that the potential nucleant particle density is similar in each liquid alloy (*i.e.*, no Mg-Al intermetallic particles form prior to the nucleation of the proeutectic α -Mg). In view of these observations, the ultrasonic grain refinement of magnesium alloys may be understood as follows using the concepts illustrated in Figure 1.

The major role of ultrasonication beyond the cavitation threshold is to increase the number of active nucleation sites, which may include both fragmented crystals and activated potential nucleating particles in the melt. However, this is insufficient to insure significant grain refinement, which requires the presence of adequate solute to enable repeated cycles of growth and nucleation from close to the ultrasonication source to areas far away from it. The hypothesis, as illustrated previously,^[2] is that once a nucleus forms and grows in an undercooled melt, a local constitutionally supercooled zone will develop. Consequently, each subsequent cycle only needs to re-establish $\Delta T_{n-\min}$, (minimum undercooling required for nucleation), rather than regenerate the total amount of $\Delta T_{n-\min}$. This requires only a fraction, $z\Delta T_{n-\min}$, of $\Delta T_{n-\min}$ to be generated. The amount of growth required is related to the length of x_{cs} in Figure 1 and this length decreases as $\Delta T_{n-\min}$ decreases. In the absence of adequate solute, ultrasonication is still able to refine the grains, but the refinement is limited to a certain extent (*e.g.*, 310 μm for pure Mg) and also restricted to areas close to the ultrasonication source.^[151] On the other hand, without ultrasonication, the alloys all solidified as coarse grain structures due to the insufficient number of repeated cycles of growth and nucleation or the large nucleation-free zone surrounding each nucleated crystal. As revealed by Eq. [4], the grain size is in fact determined by two terms, the active nucleant particle density (a physical term) and the solutal influence represented by Q (a chemical term). Significant ultrasonic grain refinement is a result of the combination of the two terms. The physical term provides the initial active nucleation sites to initiate the process, while the chemical term enables repeated cycles of growth and nucleation, along with continued cooling, until solidification is completed.

IV. DESIGN OF BIOMEDICAL ALLOYS

Typically, alloys are designed based on property criteria and only then is there a consideration of grain

refinement and how to achieve a fine grain size. A novel approach is to design the alloy so that a fine grain size is easily achieved based on the alloy chemistry. This is particularly useful in Mg alloys where grain size reduction is a large component of improving strength and formability. This was the approach taken by researchers in the development of biodegradable medical implant alloys for stent application.^[152–154]

In their case, it was more complex than just considering the as-cast grain size because as well as choosing elements that are effective at decreasing the grain size during solidification, they also needed to consider biocompatibility and being able to generate fine dispersoids that restrict grain growth during subsequent forming operations. A fine as-cast grain size also helps with obtaining a fine recrystallised grain size as recrystallized grains tend to nucleate at the as-cast grain boundaries.^[13]

Fe has the highest value of $m(k - 1)$ for magnesium alloys, but has limited solubility and more importantly is highly detrimental to corrosion. Zr is next with an $m(k - 1)$ of 29 and is a commonly used grain refiner. Zr was used, but at concentrations below which Zr particles are stable in the melt. The use of Zr also meant that elements incompatible with Zr could not be added, *e.g.*, Al (which is not biocompatible) and Si. Zn with an $m(k - 1)$ value of 2.2, Ca with 3.9, and Ag with 1.3 were therefore chosen as the key alloying elements, although in the case of these elements, it appears that in combination they have a greater effect than individually. The latter three elements also assist with precipitation during heat treatment. Y was also added to some alloys to improve corrosion resistance.^[155] Ag was later removed as it was found not to improve corrosion resistance as anticipated and Zr was removed as it was found that fine grains could be achieved without it.^[156] A number of alloys based on this system were developed and as-extruded yield strengths of above 300MPa with elongations greater than 20 pct were achieved.^[153] Alloys with good corrosion resistance had lower strengths,^[156] but all alloys had lower tension-compression anisotropies, which is at least partly due to the fine grain sizes achieved. Further improvements in yield strength were achieved by microalloying with Yb. Grain sizes of close to 100 μm were achieved during casting,^[153] which were reduced to much less than 100 μm in some modified alloys,^[154] which is a very good achievement for conventional casting operations.

V. CONCLUDING REMARKS

Since 2005, a considerable amount of research has been undertaken to both understand the mechanisms of grain refinement and to identify new grain refining technologies *via* chemical or mechanical means such as ultrasonic treatment, electromagnetic processing, or melt conditioning. Challenges remain, but we now have a much better understanding of grain formation in Mg alloys under various conditions and the mechanisms operating during grain refinement. The Interdependence Theory has identified the factors that contribute to the

final grain size. Many of these factors can be manipulated, although some are fixed through choice of casting process parameters or basic physical properties such as the diffusion coefficient.

Mg-Al alloys still present the greatest opportunity for the development of a new reliable, safe, and cost-effective refiner. The limitations to identifying such a refiner include the formation of a large nucleation-free zone during solidification and the lack of stable potent nucleant particles due to the poisoning of these particles by impurity and minor elements, such as Fe and Mn. This poisoning probably occurs by the formation of primary intermetallic phases which coat any potent nucleant particles present in the melt. While the common casting alloys continue to require the addition of Mn to deal with the corrosive effect of the Fe impurity, this problem may remain unsolved for a very long time. It appears that the only avenue is to insure the impurities form a layer with good nucleation potential. This approach may require the addition of other elements that can stabilize and convert the impurity layer to a preferred crystal structure. Assuming this is possible, the next approach is to reduce the size of the nucleation-free zone. This can best be done by increasing the potency of the nucleating substrates, which brings us back to either modifying the impurity layer or adding potent particles just before casting. Consideration of the possibly low probability of achieving a potent impurity layer suggests that the application of mechanical processes such as melt conditioning and ultrasonic treatment is a good option for achieving a fine grain size. As with the addition of chemical refiners just before casting, these mechanical methods pose a processing and economic challenge. In addition, the influence of the increased impurity content on the corrosion resistance of magnesium alloys may be a concern. However, these apparent impediments may be offset by significantly improved mechanical properties.

Mg-Zr master alloys are already a proven effective grain refining system. However, reducing the high cost and high levels of waste Zr is worth pursuing. Improvements in both factors can be addressed by choosing a master alloy with a high Zr particle number density in the 1 to 5 μm size range. Further improvements may be achieved by breaking up particle clusters, thus increasing the particle number density by processes such as melt conditioning. As with Mg-Al alloys, the nucleation-free zone significantly reduces the efficiency of the master alloy and represents a fundamental limit to further improvement.

By comparing plots of grain size vs $1/Q$ for a range of alloy compositions, one can readily show the refinement impact of any of the approaches proposed above. For example, changing the casting process from slow cooled ingot to high pressure die casting reduces the slope of the line of best fit from about 7000 to 20, while the use of Zr particles as nucleants can reduce it to 1418 without changing the solidification conditions.

Further research is required to improve the predictive capability of the Interdependence equation. For example, more accurate data are needed for D , v , and ΔT_n

and a better understanding of the influence of the casting conditions on the values of v and z .

With many of the key fundamental and practical issues resolved and better methods for analyzing grain refinement outcomes now in place, it is possible to envision some closure on the issues of consistent and maximized grain refinement of both Al-free and Al-containing alloys in the not too distant future.

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