

# **Mg Magnesium Technology 2013**

## **Plenary**

## A BRIEF HISTORY OF THE DEVELOPMENT OF GRAIN REFINEMENT TECHNOLOGY FOR CAST MAGNESIUM ALLOYS

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### Abstract

Grain size control during casting is important for ensuring the best and most consistent mechanical and corrosion performance is achieved in magnesium alloy components. Also, it is important for the fabrication of wrought Mg products with desired surface quality. Industrially, this means employing grain refinement methods. The important role of grain refinement was realized in the 1930s. However, developing a good understanding of the solidification mechanisms for improved refinement technologies involved in successful refinement has been the subject of ongoing research ever since. This paper provides a brief history of developments both scientifically and industrially, and summarizes current issues related to the development of improved grain refiners.

### Introduction

Grain refinement is essentially a nucleation process. The origins of our understanding about nucleation are well summarized by Kelton and Greer in their book 'Nucleation in Condensed Matter' [1]. As understanding of the deformation behavior of alloys improved, relationships between grain size and properties were developed such as the Hall-Petch relationship developed in the 1950s which predicts the effect of grain size on the yield strength of alloys, including Mg-Al alloys [2]. Thus the casting process itself became a focus for improving the properties of components and this was primarily achieved by stimulating the nucleation process. There are parallels between the developments of grain refining technologies for Al [3, 4] and Mg [5, 6] alloys. Both developments were first reported in the 1930s. The Al-5Ti-1B master alloy developed in the early 1970s works well for most Al alloys [3, 4]. However, for Mg alloys there is no equivalent that provides reliable, repeatable as-cast grain sizes in a cost effective manner. Since then much research effort has been focused on understanding the mechanisms of grain refinement.

Mg alloys are cast by a large variety of casting processes including ingot, sand, gravity die, low pressure die and high pressure die (HPDC) casting methods. Most Mg components produced by HPDC are Mg-Al alloys. However, complex castings for applications such as gearbox housings use precision sand casting as well as HPDC. Alloy ingot and billet are commonly produced by direct chill casting and gravity die casting. Grain refinement technology is not needed for HPDC but is important for other casting processes and can help improve creep resistance for certain Mg alloys used at elevated temperatures.

Given the limited length of a conference paper we will cover highlights rather than attempt to provide a detailed history. However, we hope that there is sufficient information provided so that the reader can gain an appreciation of the pathways followed by founders and researchers in an attempt to develop effective and reliable grain refining technologies. This paper firstly presents a summary of the range of grain refining technologies and associated mechanisms developed to explain refinement. A model that attempts to predict grain size outcomes is then described. Finally, current issues that remain unresolved are presented.

### Grain Refinement Technologies

Tables 1 and 2 summarize the key advantages and disadvantages of the developed grain refinement technologies with reference to relevant patents while Table 2 summarizes the grain refinement mechanisms proposed to explain what controls grain refinement. Table 1 is subdivided into Mg-Al alloys, Mg-Zn and RE alloys that do not contain Al, and methods applicable to all alloys.

The development of refinement technologies has more or less followed assumptions derived from observation of casting outcomes. The following puts these developments in the context of four elements, Fe, Mn, C and Zr, that underpin the assumptions used to develop particular refinement methods.

The idea of *grain refinement by Fe* stems from early work on superheating [7]. **Superheating** is an important early grain refining method developed for Mg alloys containing Al, and this process was widely used prior to and during World War II in the commercial production of Mg-Al alloys [8]. The process involves heating a Mg alloy to a temperature about 180-300 °C above its liquidus, holding it for a required period, and then cooling quickly to the pouring temperature [7]. It was believed that superheating was caused by Fe picked up from the crucible. The idea that Fe particles acted as nuclei for Mg grains resulted in the invention of an Fe inoculation process called the **Elfinal process** or FeCl<sub>3</sub> process [9]. The Elfinal process consists of plunging 0.4-1.0% of anhydrous FeCl<sub>3</sub> powder at temperatures between 740 °C and 780 °C into a molten Mg alloy [10]. The first application of the Elfinal process was on Mg-Al-Zn alloys [10] and later Al-free Mg-Zn alloys. Jessup and Petch [11, 12] of Magnesium Elektron Limited (MEL) reported that grain refinement of Mg-Zn-RE-Mn alloys was achievable using a Zn-7%Fe pre-alloy as an Fe additive replacing FeCl<sub>3</sub>. Nelson pointed out that the Elfinal process didn't work for Mg-Al alloys without Mn [8].

**Table 1. A summary of the approaches taken to grain refine Mg alloys with the advantages and disadvantages of each approach.**

Process	Advantages	Disadvantages
<b>Mg – Al alloys</b>		
Solute additions	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. Alloy composition changes and mechanical properties may not be desirable.
Superheating	Significant grain refinement can be achieved.	Difficult to control. High temperatures (~850°C) must be used that can cause melt handling problems. Not clear what the nucleant particles are.
Elfinal	Produces a degree of refinement.	Adds Fe which decreases corrosion resistance. Chlorine is produced which has health implications.
C inoculation	Significant grain refinement can be achieved.	The only approach used commercially at this stage. However, the most effective way of adding C is under debate.
Native grain refinement	The native particles present in high purity melts are more potent than those present in commercial alloys.	No direct evidence of particles and their composition. Pure alloys are more expensive. Limited to Mg-Al based alloys.
SiC	Works reasonably well.	Grain refinement is not as effective as desired. Also, SiC is unstable in the melt and appears to be another C-inoculation technique.
Fe, Mn, Ti additions	Reported that some grain refinement achieved. However, poisoning occurs when Fe and Mn are both present.	Results vary suggesting that the reason for the grain refinement cannot be controlled. It is not understood completely why they work.
Borides	These are known nucleants in Al-based alloys and are available as master alloys. Reports of good grain refinement.	Borides have been tried in CAST and other work and have been found to show inconsistent results. Settling of particles is an issue for commercial application.
AlN, ZnO	Crystallographic edge-to-edge matching ( <i>e2em</i> ) predicts AlN and ZnO are possible nucleants.	ZnO is unstable in melts and a previous attempt at using AlN particles did not perform as well as expected.
High pressure die casting	High cooling rate driven grain refinement without any change of alloy chemistry.	Not suited for the production of basic shapes (billet and slab); having dendritic grains in most cases.
<b>Mg – Zn, RE alloys that do not contain Al, Mn, Si, Fe</b>		
Mg-Zr master alloys	Very effective, producing grain sizes down to < 50 microns.	Expensive, high degree of waste Zr in sludge that forms from settling of Zr particles. Reaction with Fe-based crucibles can also consume Zr. Large agglomerates affect mechanical integrity of castings.
Al additions	Small Al additions appear to grain refine some Mg-RE alloys through the formation of pro-peritectic Al <sub>2</sub> RE particles that act as nuclei.	More information is required on which alloys this approach can be applied to and the subsequent effect on properties.
<b>Applicable to all Mg alloys</b>		
Ultrasonic Treatment	Depending on the alloy composition Ultrasonic Treatment can significantly reduce the grain size.	Ultrasonic transducers do not function at elevated temperatures and ultrasonic attenuation is a concern. May not be as effective for large castings.
Electromagnetic stirring	An effective and clean process that can produce fine grain sizes.	Electromagnetic equipment adds cost. The process appears to be more suited to casting basic shapes (billet and slab) rather than components.
Melt Conditioning	Melt conditioning is able to increase the number of nucleation events, significantly reducing the grain size.	Melt conditioning equipment adds cost to casting process. More data is needed on the performance of castings produced this way.

In 1945 Tiner [13] studied the superheating of Mg alloys and the influence of Fe and Mn on the response of superheating. He found that Fe favours grain refinement by superheating. Partridge [14], in 1948, observed obvious grain refinement of Mg-Al alloys using a new but slightly rusty mild steel crucible. He concluded that the loosely adherent rusty Fe had produced the observed grain-refining effect. Emley [5], however, suggested that the observed grain refinement was due to the uptake of carbon from the

crucible, as the surface layer of a new mild steel crucible contains more carbon than does the surface layer of a repeatedly used crucible. Regarding the Elfinal process, Emley suggested that Fe containing intermetallic particles or Al carbide (Al<sub>4</sub>C<sub>3</sub>) particles were possibly the nucleants [5]. Emley apparently preferred the Al<sub>4</sub>C<sub>3</sub> hypothesis, as he believed that the hydrolysis of FeCl<sub>3</sub> gave rise to copious HCl fumes, which could attack steel crucibles to liberate carbon from the surface layers [5].

Tamura et al. [15] found that the presence of Fe increases the grain size of high purity AZ91E alloys. They presented evidence showing that the ternary Al-C-O particles, which are thought to be effective nucleants, would transform to ineffective quaternary Al-C-O-Fe compounds in the presence of Fe [15]. They thus concluded that Fe was an inhibiting element for the grain refinement of Mg-Al alloys, as it poisoned the potency of the Al-C-O nucleants by transforming them to Al-C-O-Fe [15]. Gao et al. [16] then found that the grain size of scrap AZ91 decreased with decreasing Fe content from 0.024% to 0.0009%, and suggested that Fe acts as an inhibiting element for grain refinement. This apparently contradicts the basis of the Elfinal process. On the other hand, it is interesting to note that although the Elfinal process has been known since the early 1940s [8-10, 17, 18], no micrographs or data can be found in the literature (including the original patent on this process [10]) as to the effectiveness of this process. It is likely that some experiments were conducted but for some reason the results were not published.

The influence of Fe on the grain refinement of high purity Mg-Al alloys was investigated using various methods of Fe addition [19, 20]. The addition of Fe in the form of anhydrous FeCl<sub>3</sub> produced obvious grain refinement in high-purity Mg-3%Al and Mg-9%Al alloys. Grain refinement could also be achieved through the uptake of Fe from the crucible surfaces; however, the addition of Fe in the form of ALTAB<sup>TM</sup> Fe75 compact did not cause grain refinement. The use of anhydrous FeCl<sub>3</sub> also leads to grain refinement in high-purity Mg-Al alloys when these alloys are melted in carbon-free aluminium titanite crucibles, suggesting that the Elfinal process has little to do with the Al<sub>4</sub>C<sub>3</sub> hypothesis proposed by Emley. In contrast, Fe- and Al-rich intermetallic particles were observed in many Mg grains when the Elfinal process was used, suggesting that these particles are possibly nucleants for Mg grains.

The above contradictions illustrate the problem in understanding the mechanisms operating during solidification. Although the use of Fe results in good grain refinement via the Elfinal process [10-12], it has been found that Mg-Al alloys with ultra-low levels of Fe have a naturally fine grain size compared to similar alloys that contain normal impurity levels of Fe. Taking another approach Nelson [8] observed that AZ92 and AZ63 alloys containing <0.001% Fe had a finer grain size than the same alloys containing 0.02% Fe. Tamura et al. [15, 21, 22] confirmed Nelson's observations. The grain refinement by control of impurity levels is referred to as **native grain refinement**. They also showed particles containing Al, C and O in the central regions of certain Mg grains in high purity Mg-Al alloys and attributed native grain refinement to the presence of Al<sub>4</sub>C<sub>3</sub> or Al-C-O particles.

Native grain refinement was observed exclusively in high purity Mg-Al alloys. The grain size of Mg-9%Al alloys was found to increase with increasing proportion of commercial purity up to 100% Mg [20]. Little Fe and Mn is present in the high purity Mg-Al alloys and as there was no uptake of any other impurities from the crucible used in this study, it was assumed that the nucleant particles involved in native grain refinement of Mg-Al alloys are Al<sub>4</sub>C<sub>3</sub> or Al-C-O particles as concluded by Tamura et al [15, 22]. In commercial purity Mg-Al based alloys the presence of Fe or Mn degrades the potency of Al<sub>4</sub>C<sub>3</sub> or Al-C-O by forming quaternary Al-C-O-Fe or Al-C-O-Mn compounds.

Investigations conducted since the 1930s have been unable to provide consensus on the **influence of Mn on the grain refinement** of Mg-Al alloys. It was believed that superheating is very closely related to the presence of impurity elements such as Fe, Mn and C, in the alloy melts. Tiner [13] found that high-purity Mg-Al alloys with Mn content less than 0.02% showed no appreciable superheating effect, while Mg-Al alloys containing 0.19% or more Mn demonstrated some grain refinement during superheating. Tiner [13] further claimed that binary Mg-Al alloys that can be refined by superheating need to contain either Fe or Mn in excess of their solubilities at the liquidus temperature of the alloy. Nelson [8] subsequently investigated the grain refinement of an AZ92 (Al: 9% and Zn: 2%) alloy with 0.4% or more Mn, and found that alloys with such a high Mn content could not be grain-refined by superheating unless the excessive Mn was settled out by holding at low temperatures (650 – 700°C) and then removed from the melt by sludging out. Nelson's [8] observations contradict Tiner's [13], who obtained full grain refinement in Mg-9%Al alloy containing 0.98% Mn.

Tamura et al. [15, 22] re-examined the influence of minor impurity elements on the grain refinement of high purity Mg-9%Al alloys (Fe < 0.001%; Mn < 0.001%). They used an Al-10%Mn master alloy to add Mn. Contrary to Tiner's observations, Tamura et al. [15] found that the average grain size of a chill bar sample increased progressively from about 40 µm to 160 µm with increasing Mn content from less than 0.001% to 0.47%, where Fe was kept as low as 0.002%. Al-C-O particles were observed in the Mg grains before Mn additions. However, it was found that, in the presence of Mn, these ternary particles transformed to quaternary Al-C-O-Mn. Tamura et al. [15] therefore concluded that Mn was a grain refinement inhibitor, as it poisoned the potency of the Al-C-O nucleants by transforming them into Al-C-O-Mn. Particles that contained Al, Mn, Fe, O, and occasionally Si, were also observed at the centers of Mg grains. To add to the complexity of the effect of Mn, they later published an article about the formation of Mn-containing particles in a commercial AZ91E alloy using a single-roll rapid solidification method [23]. Interestingly, they found that cross-shaped Al-Mn(-Fe) particles were frequently observed when the AZ91E melt was rapidly cooled from superheating temperatures (e.g. 900 or 950°C) to 700°C. They then claimed that the cross-shaped Mn-containing particles produced effective nucleation sites for Mg grains. These conclusions differ from those they made before, where they claimed that the nucleant particles are Al-C-O particles and that Mn is a poisoning element for the grain refinement of Mg-Al alloys. Byun et al. [24] observed the existence of Al<sub>8</sub>(Mn,Fe)<sub>5</sub> particles within the α-Mg grains in an AZ91 slurry sample containing 0.23% and more Mn, suggesting that Al<sub>8</sub>(Mn,Fe)<sub>5</sub> particles act as the heterogeneous nucleation sites. On the basis of Mn solubility calculations, Byun et al. [24] suggested that high Mn concentrations favour grain refinement because supersaturated Mn is likely to precipitate to form Al<sub>8</sub>(Mn,Fe)<sub>5</sub> particles where primary Mg grains nucleate.

A recent study [25] showed that the addition of 0.1% to 1.0% Mn introduced in the form of an Al-60%Mn master alloy splatter, resulted in obvious grain refinement of high purity Mg-3%Al, Mg-6%Al and Mg-9%Al, as well as commercial AZ31 alloys. The majority of the Mn-containing particles observed in the commercial AZ31 base alloy were of the Al<sub>8</sub>Mn<sub>5</sub> type, whereas after addition of extra Mn the predominant group of intermetallic particles changes to the ε-AlMn type. The metastable hexagonal ε-AlMn phase is likely to be a more effective nucleant for Mg

grains than the stable rhombohedral  $Al_8Mn_5$ . It was proposed that the increase in grain size after a long time of holding at a given melt temperature is due to the transformation of the metastable  $\epsilon$ - $AlMn$  to the stable  $Al_8Mn_5$ . This hypothesis for grain refinement by Mn can also explain the mechanism of grain refinement by superheating.

To overcome the shortcomings of the superheating process (e.g. high operating temperature and applicability to small melts only), post-war research of grain refinement of Mg alloys shifted to developing an alternative method applicable to large melts and at lower operating temperatures. These efforts led to the discovery of the **carbon refining process** [26, 27].

In principle, any materials containing carbon can be used as inoculating additives, and do have a grain-refining effect when properly inoculated. These additives can be categorized into three groups: carbonaceous gases, solid carbon additives and organic chlorides. The use of carbon monoxide (CO) or carbon dioxide ( $CO_2$ ) was first reported in a US patent [28] to give satisfactory grain refinement when bubbled through the melt. Subsequently a number of carbonaceous gases were reported to have a grain-refining ability to Mg alloys, such as acetylene, methane, and natural gas [8, 27, 29-31]. Solid carbon additives include carbon powder, lampblack, magnesite [28], calcium carbide [32, 33], calcium cyanamide, paraffin wax, silicon carbide [34, 35].

From an operational aspect, the carbonaceous gases and organic chlorides can be more easily introduced into Mg melts than the solid carbon additives. In addition, bubbling a melt also helps to degas the melt. The addition of carbon in the form of  $C_2Cl_6$  or  $Cl_2-CCl_4$  blend was widely used before the 1970s because of the combined action of grain refining and degassing. The major problem of using carbonaceous gases, particularly chlorine-based gases, is the emission of chlorinated hydrocarbons (CHC). Considerable efforts have been made to produce a commercially reliable carbon-based grain refiner for Mg-Al alloys. For example, Renger and Simon [36] reported an effective grain refiner named Nucleant 5000, which appeared to work satisfactorily on AZ91 alloys. Waxfluorspar-carbon grain refiners were developed early in England [37] and in Canada [38]. Liu et al. [39] reported an  $Al_4C_3$ -SiC-Al alloy suitable for grain refinement of Mg-Al alloys such as AZ31 and AZ63. Motegi et al. [40, 41] disclosed a carbon grain refiner that contains either pure carbon powder or a mixture of carbon and  $Nb_2O_5$  or  $V_2O_5$  powder. However, to date carbon-based grain refiners prove unreliable and produce inconsistent grain refinement in Mg-Al alloys.

There have been many other particles tried in Mg-Al alloys including borides [42, 43], ZnO [44] and AlN [45]. This is understandable because the presence of foreign particles will always tend to facilitate the heterogeneous nucleation of Mg grains as long as they are not completely unwettable. Whilst many of these particles have shown promise there is usually an issue to do with their use, be it instability in the melt, rapid settling or that the grain refinement efficiency is not sufficient enough.

Table 2 groups the mechanisms of grain refinement in Mg-Al alloys into four categories, solute additions, impurity poisoning, C additions and other nucleant particles. A recent review [6] by the authors has shown that broadly all of the grain refining techniques that have been proposed so far can be grouped into one of these categories. This begins to simplify the issues related to grain

refinement of Mg-Al alloys, but more work is required to confirm these hypotheses.

The only commercially successful technology is **Zr grain refinement by Mg-Zr master alloys** while carbon inoculation is sometimes used for sand and gravity die casting of Rare Earth (RE) alloys for aerospace and automotive applications [5]. Zr 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  $Al_3Zr$ . Some research has been undertaken to understand why Zr is such a remarkably effective grain refiner, although further work is required to optimize these alloys. It has been shown that the performance of Mg-Zr master alloys is related to the Zr particle number density of particles less than 5 microns in size as the larger particles settle out during alloying [46, 47]. Recently, it has also been shown that small Al additions are able to effectively grain refine some Mg-RE containing alloys [48].

There is increasing interest in processes that may assist the nucleation of grains such as Ultrasonic Treatment (UT) and Melt Conditioning. The results to date have shown that they are effective in producing considerable refinement. However, little industrial application has occurred to date and thus the focus of future research is on their practical implementation in casting operations [49].

More details on research into the grain refinement of Mg alloys undertaken to date can be found in two reviews by the authors [50].

### Theoretical Developments

As highlighted in the previous section and Tables 1 and 2, the proposed theories of grain refinement of Mg alloys have essentially been explanations of the observed, and often contradictory, refinement effects with little definitive evidence of particle characteristics such as type and size distribution. The underlying assumptions such as the role of Fe and the presence of C, were used to develop new refining methods. There has been much effort focused on identifying potential nucleant particles [51] or speculation on the type of native or impurity nucleant particles [20]. It is known that grain size is affected by the Al content in Mg-Al alloys but alloy composition was not taken into account when analyzing grain refinement outcomes until about 2005 [50].

In 2001 a theory was proposed that brought together alloy constitution and particle potency showing that grain size is related to the growth restriction factor  $Q$  [52]. The recent Interdependence Model, equation 1, is a rigorous predictive equation that highlights the factors affecting the as-cast grain size and it incorporates elements of the Free Growth Model [53] developed in the 1990s for the calculation of  $\Delta T_n$ , the undercooling required for nucleation on a particle of a particular size [54].

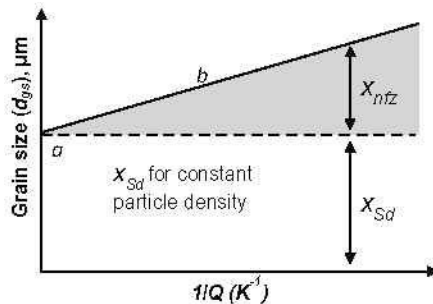
$$d_{gs} = \frac{D \cdot z \cdot \Delta T_{n-min}}{v \cdot Q} + \frac{4.6 \cdot D}{v} \left( \frac{C_l^* - C_o}{C_l^* \cdot (1 - k)} \right) + x_{sd} \quad (1)$$

where  $D$  is the diffusion coefficient,  $v$  the rate of growth of the solid-liquid (S-L) interface,  $C_l^*$  the composition of the liquid at the S-L interface at  $x_{cs}$ ,  $\Delta T_{n-min}$  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

**Table 2. A summary of the theories proposed to explain the mechanisms of grain refinement of Mg alloys with the weaknesses of each theory.**

Process	Related approaches	Future Considerations
<b>Mg – Al alloys</b>		
Solute additions	It is well established that growth restriction by alloying elements contributes to grain size reduction. However, it should be noted that alloys that show a high growth restriction effect may not always be commercially attractive or useful.	Lack of physical data to ensure reliable prediction of grain size using the developed predictive equations. It is also clear that whilst this is a significant effect it is not the most important one, particularly in casting alloys.
Impurity poisoning	It appears that the superheating effect, the Elfinal process and Native grain refinement are all related to the effect of impurities precipitating on the surface of particles.	Whilst there is circumstantial evidence for this occurring, it is difficult to obtain direct evidence. Also the wide variety of effects means that it is difficult to explain all observations using this approach.
C inoculation and SiC	Carbon-based inoculants are the most effective nucleants known and the ones that are used commercially. There have been many different approaches proposed. A recent breakthrough has been the understanding that carbon reacts with Al to form $Al_4C_3$ particles and $Al_2MgC_2$ which can both act as nuclei. $Al_2CO$ may be a nucleant in some situations.	An effective commercial approach has not as yet been able to be developed and the effectiveness of grain refinement is significant rather than very good.
Other nucleant particles	No other attractive nucleants have been identified yet, despite many trials.	A potent nucleant such as Zr for Al-free Mg alloys may exist or may not. However, given the commercial importance of Mg-Al based alloys, it is worth further effort to identify a potent grain refiner for these alloys.
<b>Mg – Zn, RE alloys that do not contain Al, Mn, Si, Fe</b>		
Mg-Zr master alloys	Both soluble and insoluble Zr contribute to grain refinement.	Prediction capability to take into account simultaneous increases in solute Zr and Zr particle number density needs further refinement.
Al additions	Small Al additions appear to grain refine some Mg-RE alloys through the formation of pro-peritectic $Al_2RE$ particles that act as nuclei.	More information is required on which alloys this approach can be applied to and the subsequent effect on properties.
<b>Applicable to all Mg alloys</b>		
Mechanical approaches	Includes approaches such as ultrasonic treatment, electromagnetic stirring processes and melt conditioning.	For most of these approaches there is no agreed theory. Depending on the technique, issues such as cavitation and fragmentation of impurity particles and $\alpha$ -Mg grains are proposed as generators of many nucleants.

nucleation event as the temperature gradient moves towards 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  $(C_l(x) - C_0)/(C_l^* - C_0) = 1\%$  [54].



**Figure 1:** Representation of a grain size vs  $1/Q$  plot showing the contribution of the nucleation-free zone  $x_{nfz}$  and the distance to the next most potent particle  $x_{sd}$  to the final as-cast grain size.

The first two terms in equation 1 are determined from the alloy characteristics and the casting conditions defining the formation

of the nucleation-free zone ( $x_{nfz}$ ) as insufficient CS is developed within this zone to cause a nucleation event to occur [54]. Figure 1 illustrates the change in  $x_{nfz}$  with  $Q$  highlighting that for low solute alloys  $x_{nfz}$  significantly restricts refinement by preventing nucleation on suitable particles. The third term  $x_{sd}$  is defined by the distance to the next most potent particle, assumed to be constant in Figure 1. The value of  $x_{sd}$  can be decreased by increasing the particle number density, for example, by adding more Zr master alloy.

Plots of the measured grain size vs  $1/Q$  present a straight line that provides a useful tool for the analysis of the mechanisms of grain refinement and has been successfully applied to Al, Ti and Mg alloys [54, 55]. The application of the grain size vs  $1/Q$  plots has revealed the mechanisms of refinement. For example, superheating of commercial Mg-Al alloys and native refinement of high purity alloys are related [20, 56]. It now appears that superheating removes the effect of impurities allowing the more potent native nucleants whether they are carbides or oxide particles, to be available for nucleation thus producing a finer grain size. Also, a comparison of high and commercial purity Mg-Al alloys has highlighted that a major factor controlling grain size

is the nucleation-free zone which reflects the effect of alloy chemistry ( $Q$ ) in producing large grain sizes for AZ31 and finer sizes for AZ91 [54]. It has also shown the improvements in nucleation efficiency on the addition of SiC to Mg-Al alloys [57].

These plots have been applied to analyzing the performance of Mg-Zr master alloys showing that Zr particle number density is the key factor differentiating different types of master alloy [46, 47]. Also, the linear form of  $d_{gs}$  vs  $1/Q$  has been shown to apply to a wide range of casting conditions and the application of Ultrasonic Treatment highlighting the important role of  $Q$  [6].

### Issues Remaining

Current understanding can be summarized as: (1) high purity Mg-Al alloys exhibit native grain refinement with Al carbide or oxide particles being the nucleant particles and addition of either Fe or Mn individually leads to further refinement; (2) commercial Mg-Al alloys exhibit poor refining performance due to an interaction between Al, Fe and Mn forming an intermetallic layer of lower nucleation potency on the native nucleants; (3) Zr remains the best refiner for Mg-Zn and -RE alloys without Al. However, there is no ideal grain refining technology for Mg alloys. Even the superior Mg-Zr master alloy produces sludge wasting considerable Zr that does not contribute to refinement. In almost every case there are issues with commercial implementation and considerable gaps in our knowledge of the mechanisms of grain refinement.

For Mg-Al alloys poisoning by impurity and minor elements appears to be a major issue preventing the development of a reliable grain refiner and it is probable that a different approach to developing a grain refining system is needed. For all Mg alloys the formation of a nucleation-free zone reduces grain refining performance particularly in lean alloys. Strategies for tackling these issues are discussed in a recent publication [6].

The recent investigations of mechanical methods such as ultrasonic treatment, electromagnetic stirring and melt conditioning show promise. However, proving that these methods will be practical and cost effective for industrial application is an important next step.

Research on the grain refinement of Mg alloys has been very active but that has been largely driven by researchers in universities and institutes over the last two decades. Closer collaboration between academia and industry will help address these issues and more importantly, increase the impact on industrial practice.

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