2013
Magnesium Technology
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Magnesium was produced first in 1808, more than 200 years ago, by Sir Humphry Davy. It took a few decades to develop and establish stable production processes, and in the middle of the 19th century magnesium was available in larger quantities and ready to be used. In fact it met a new technology at these times: photography. Magnesium was utilized in flashlights and this endured until the end of the 20th century. Of course, flashlights are not a structural application. But with time in the early years of the 20th century again a step in the technical development took place: the Wright brothers started to fly. It was found out early that wooden airplanes would not do their job at all. Light metal alloys had to be used, and magnesium alloys were part of aeronautics from the beginning. In fact an engine for aircrafts made out of a magnesium alloy was shown 1909 in Frankfurt, Germany, at the first "Internationale Luftschiffahrt Ausstellung," the first international aerospace exhibition. While magnesium was important for aerospace 100 years ago, today it is still looking for acceptance in aerospace industries.

In contrast to the slight acceptance in aerospace, magnesium alloys are fairly well accepted in automotive industries as well as for consumer, computer, and communication applications. Due to its excellent specific properties magnesium alloys can compete especially in transportation with aluminium and even with steel leading to tremendous weight savings. This directly leads either to an increase in payload or a fuel reduction (saves money for the end user), or reduces greenhouse gas emissions. Today automotive industries are showing lots of examples for the use of magnesium alloys in various applications, but an average standard car only contains a few kilograms of magnesium alloys. To enhance the use of magnesium even in this field it is still necessary to develop alloys and to optimize processes.

The development of processes for primary production, alloy development and the processing routes started in the early 20th century and continued over the years. Several authors compiled the state of the art. Among them are J. L. Haughton and W. E. Prytherch (1938), A. Beck (1939, reprinted 2001), L. M. Pidgeon, et al. (1946), W. H. Gross (1949), G. V. Raynor (1959), C. S. Roberts (1960), E. F. Emley (1966), R. S. Busk (1986), and in recent years M. A. Avedesian and H. Baker (1999), C. Kammer (2000), K. U. Kainer (2003), and H. F. Friedrich and B. L, Mordike (2004). In all of these books the state of the art is shown and the progress in magnesium alloy and technology development is described. But these books only present a view into the past.

The first Magnesium Technology symposium at the TMS meetings took place at the TMS Annual Meeting in Nashville, Tennessee, 2000. Since this time the symposium is showing the lively research of the active magnesium community in the world and it presents also a look into the future. This year is the 14th edition of this meeting, and it will be held in San Antonio, Texas, from March 3-7, 2013. The symposium is arranged into an opening plenary session and a number of technical sessions which address the full scope of Magnesium research and development. These sessions include primary production, casting and solidification, deformation mechanisms and texture, alloy and microstructural design, corrosion, high temperature behaviour, processing-microstructure-property relationships, and advanced processing and joining.
Last, the organizing of these proceedings would not have been possible without the dedication and assistance of TMS staff. In particular, we would like to recognize Ms. Patricia Warren for her tireless patience and hard work.

Over the past 13 years, the Magnesium Technology proceedings, through its high quality technical content, has become the primary proceedings for the magnesium industry and technical community. We hope that this year’s volume will serve you just as well.

Norbert Hort (Helmholtz-Zentrum Geesthacht, Germany)
Suveen N. Mathaudhu (U.S. Army Research Office, USA)
Neale R. Neelameggham (IND LLC, USA)
Martyn Alderman (Magnesium Elektron, UK)
ABOUT THE LEAD EDITOR

Norbert Hort
MAGNESIUM TECHNOLOGY 2013 LEAD EDITOR

Norbert Hort is the head of the Magnesium Processing Department at the Magnesium Innovation Centre (MagIC) within the Helmholtz-Zentrum Geesthacht Zentrum für Material- und Küstenforschung, Geesthacht, Germany (formerly the GKSS Research Centre). Concurrently he is lecturer at the Leuphana University, Lüneburg, Germany. He studied Materials Sciences at the Clausthal University of Technology (CUT), Germany, where he has been involved in magnesium research since the early 1990s. His diploma thesis (1994) dealt with gas-atomized, hot-extruded magnesium alloys. During 1994-95 he worked as a researcher at the Institute of Materials Sciences (CUT) and he joined the HZG in 2000. He got his Ph.D. degree in Materials Sciences in 2002 from the Clausthal University of Technology. In the MagIC he is responsible for the development of new creep resistant magnesium alloys, grain refinement and the castability of magnesium alloys (viscosity and density of melts, fluidity, and mould filling). A major focus of his research is the development of new magnesium alloys for biodegradable implants in a close collaboration with biologists and clinicians. He is co-author of more than 150 peer reviewed journal papers and contributions to conference proceedings. In recent years he was involved in the organizing committees of the conference series “Magnesium Alloys and their Applications” and of the conference “Light Metal Technologies 2011.” - Since 2009 he also has been the chairman of the technical committee “Magnesium” of the German Society of Materials (DGM).
ABOUT THE EDITORS

**Suveen Nigel Mathaudhu** serves as the Program Manager for Synthesis and Processing of Materials with the U.S. Army Research Office (ARO), Materials Science Division. He received his B.S.E. in Mechanical Engineering from Walla Walla University in 1998, and Ph.D. in Mechanical Engineering from Texas A&M University in 2006. In his current position, he manages programs which focus on the use of innovative approaches for processing high performance structural materials reliably and at lower costs. He also concurrently serves as an Adjunct Assistant Professor in the Department of Materials Science and Engineering at North Carolina State University, where his research interests include ultrafine-grained and nanostructured materials by severe plastic deformation, consolidation of metastable particulate materials and processing-microstructure-property relationships of refractory metals and lightweight metals, and thermally stable nanocrystalline materials. He has co-authored over 60 technical publications in these areas.

**Neale R. Neelameggham** is ‘Guru’ at IND LLC, involved in technology marketing and consulting in the field of light metals and associated chemicals, [boron, magnesium, titanium, lithium and alkali metals], rare earth elements, battery and energy technologies, etc. He has over 38 years of expertise in magnesium production technology from the Great Salt Lake brine in Utah. He was involved in Process Development of its startup company, NL Magnesium, through the presently known US Magnesium LLC and was its Technical Development Scientist from where he retired. Dr. Neelameggham’s expertise includes all aspects of the magnesium process, from solar ponds through the cast house including solvent extraction, spray drying, molten salt chlorination, electrolytic cell and furnace designs, lithium ion battery chemicals and byproduct chemical processing. In addition, he has an in-depth and detailed knowledge of alloy development as well as all competing technologies of magnesium production, both electrolytic and thermal processes worldwide. Dr. Neelameggham holds 13 patents and a pending patent on boron production, and has several technical papers to his credit.

As a member of TMS, AIChE, and a former member of American Ceramics Society, he is well-versed in energy engineering, bio-fuels, rare-earth minerals and metal processing, and related processes. Dr. Neelameggham has served in the Magnesium Committee of LMD since its inception in 2000, chaired it in 2005, and has been a co-organizer of the Magnesium symposium since 2004. In 2007 he was made a permanent co-organizer for the Magnesium symposium. He has been a member of the Reactive Metals Committee and Recycling Committee, and a Programming Committee representative of LMD. In 2008, LMD and EPD created the Energy Committee following the symposium on CO₂ Reduction Metallurgy symposium initiated by him. Dr. Neelameggham
was selected as the inaugural Chair for the Energy Committee with a two-year term. He received the LMD Distinguished Service Award in 2010 and has been a co-editor of the Energy Technology symposium proceedings volume. Dr. Neelameggham holds a doctorate in extractive metallurgy from the University of Utah.

Martyn Alderman is Divisional Director of Technology for the Magnesium Elektron Group Worldwide. He obtained a Masters Degree in Material Science from the University of Cambridge (United Kingdom) in 1979 and for the next 20 years he worked in aluminium rolling mills producing and developing Al-Cu-Zr, Al-Mn, Al Mg-Mn, Al-Zn-Mg, and Al-Li-Cu alloys for Superplastic forming. He also has significant operational experience direct chill casting and in the extrusion of high strength aluminium alloys.

In 2003 he joined Magnesium Elektron during the acquisition of their large Madison, Illinois rolling operation in the United States. For the next few years he was travelling between the United States and Europe encouraging the wider use of magnesium sheet in transport applications, in particular by use of superplastic forming, and later in managing the post acquisition integration of the Revere North American Graphic Arts business. He chaired the 2010 International Magnesium Association Conference in Hong Kong, and for the past two years had been involved in editing and producing a 270 page Handbook on Designing with Magnesium Alloys.

As a member of TMS, SAE, and AMS, he is a regular attendee at worldwide magnesium conferences keeping abreast of global technology development with the aim of maintaining the Magnesium Elektron’s position as a world leader in magnesium alloys and their end use applications.
## MAGNESIUM TECHNOLOGY 2013
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Magnesium Technology 2013

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

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Keywords: Magnesium, Grain refinement, Solidification

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-STI-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 FeCl₃ process [9]. The Elfinal process consists of plunging 0.4-1.0% of anhydrous FeCl₃ 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 FeCl₃. Nelson pointed out that the Elfinal process didn’t work for Mg-Al alloys without Mn [8].
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 \((\text{Al}_4\text{C}_3)\) particles were possibly the nucleants [5]. Emley apparently preferred the \(\text{Al}_4\text{C}_3\) hypothesis, as he believed that the hydrolysis of \(\text{FeCl}_3\) gave rise to copious \(\text{HCl}\) 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 FeCl3 produced
obvious grain refinement in high-purity Mg-3%Mg and Mg-9%Mg
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™ Fe57 compact did not cause grain
refinement. The use of anhydrous FeCl3 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 Al4C3 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 Al4C3 or Al-C-O
particles.

Native grain refinement was observed exclusively in high purity
Mg-Al alloys. The grain size of Mg-9%Mg 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 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
Al4C3 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 Al4C3 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%Mg 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%Mg 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 presence of Al4(Mn,Fe)5 particles within the α-Mg
grains in an AZ91 slurry sample containing 0.23% and more Mn,
suggesting that Al4(Mn,Fe)5 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 Al4(Mn,Fe)5 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%Mg,
Mg-6%Mg and Mg-9%Mg, as well as commercial AZ31 alloys.
The majority of the Mn-containing particles observed in the
commercial AZ31 base alloy were of the AlMn type, whereas
after addition of extra Mn the predominant group of intermetallic
particles changes to the α-AlMn type. The metastable hexagonal α-
AlMn phase is likely to be a more effective nucleant for Mg
grains than the stable rhombohedral $\text{Al}_2\text{Mn}$, 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 ε-AlMn to the stable $\text{Al}_2\text{Mn}$. 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, magnetite [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$_6$Cl$_6$ or C$_3$Cl$_6$ 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. This hypothesis for grain refinement by Mn can also explain the mechanism of grain refinement by superheating.

Renger and Simon [36] reported an effective grain refiner named Nucleant 5000, which appeared to work satisfactorily on AZ91. This hypothesis for grain refinement by Mn can also explain the mechanism of grain refinement by superheating.

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$_2$Zr. 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 $\Delta T_{uc}$, the undercooling required for nucleation on a particle of a particular size [54].

$$
\Delta T_{uc} = \frac{D \cdot \tau \cdot \Delta T_{uc-min}}{v \cdot Q} + \frac{4.6\cdot D}{v} \left( \frac{C_i' - C_p}{C_i' \cdot (1 - k)} \right) + x_{sd}
$$

where $D$ is the diffusion coefficient, $v$ the rate of growth of the solid-liquid (S-L) interface, $C_i'$ the composition of the liquid at the S-L interface at $x_{sd}$, $\Delta T_{uc-min}$ the undercooling required for nucleation on the largest available particle, and $\Delta T_{uc-min}$ is the incremental amount of undercooling required to activate the next
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 \((C_f(\alpha')) - C_{df}/(C^*_f - C_{df}) = 1\%\) [54].

Figure 1: Representation of a grain size vs 1/Q plot showing the contribution of the nucleation-free zone \(x_{df}\) and the distance to the next most potent particle \(x_{n2}\) 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 \(x_{df}\) as insufficient CS is developed within this zone to cause a nucleation event to occur [54]. Figure 1 illustrates the change in \(x_{df}\) with Q highlighting that for low solute alloys \(x_{df}\) significantly restricts refinement by preventing nucleation on suitable particles. The third term \(x_{n2}\) is defined by the distance to the next most potent particle, assumed to be constant in Figure 1. The value of \(x_{df}\) 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

<table>
<thead>
<tr>
<th>Process</th>
<th>Related approaches</th>
<th>Future Considerations</th>
</tr>
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<tbody>
<tr>
<td>Solute additions</td>
<td>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.</td>
<td>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.</td>
</tr>
<tr>
<td>Impurity poisoning</td>
<td>It appears that the superheating effect, the Elfmal process and Native grain refinement are all related to the effect of impurities precipitating on the surface of particles.</td>
<td>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.</td>
</tr>
<tr>
<td>C inoculation and SiC</td>
<td>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 Al2C3 particles and Al2MgC4 which can both act as nuclei. Al2CO may be a nucleant in some situations.</td>
<td>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.</td>
</tr>
<tr>
<td>Other nucleant particles</td>
<td>No other attractive nucleants have been identified yet, despite many trials.</td>
<td>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.</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>Process</th>
<th>Related approaches</th>
<th>Future Considerations</th>
</tr>
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<tbody>
<tr>
<td>Mg – Al alloys</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Zr master alloys</td>
<td>Both soluble and insoluble Zr contribute to grain refinement.</td>
<td>Prediction capability to take into account simultaneous increases in solute Zr and Zr particle number density needs further refinement.</td>
</tr>
<tr>
<td>Al additions</td>
<td>Small Al additions appear to grain refine some Mg-RE alloys through the formation of pro-peritectic Al2RE particles that act as nuclei.</td>
<td>More information is required on which alloys this approach can be applied to and the subsequent effect on properties.</td>
</tr>
<tr>
<td>Mechanical approaches</td>
<td>Includes approaches such as ultrasonic treatment, electromagnetic stirring processes and melt conditioning.</td>
<td>For most of these approaches there is no agreed theory. Depending on the technique, issues such as cavitation and fragmentation of impurity particles and α-Mg grains are proposed as generators of many nucleants.</td>
</tr>
<tr>
<td>Mg – Zn, RE alloys that do not contain Al, Mn, Si, Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Applicable to all Mg alloys</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 $d_{p}$ 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 AI. 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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