

The Role of Solute in Grain Refinement of Magnesium

Y.C. LEE, A.K. DAHLE, and D.H. StJOHN

The effect of separate solute additions of Al, Zr, Sr, Si, and Ca on grain size of Mg has been investigated. Increasing the Al content in hypoeutectic Mg-Al alloys resulted in a continuous reduction in grain size up to 5 wt pct Al, reaching a relatively constant grain size for higher Al contents (above 5 wt pct). The effect of Sr additions was investigated in both low- and high-Al content magnesium alloys, and it was found that Sr had a significant grain refining effect in low-Al containing alloys but a negligible effect on grain size in Mg-9Al. Additions of Zr, Si, and Ca to pure magnesium resulted in efficient grain refinement. The grain refinement is mainly caused by their growth restriction effects, *i.e.*, constitutional undercooling, during solidification, but the effect of nucleant particles, either introduced with the alloying additions or as secondary phases formed as a result of these additions, may enhance the grain refinement. A brief review of grain refinement of magnesium alloys is included in this article to provide an update on research in this field.

I. INTRODUCTION

WORLD production of magnesium, the eighth most common element in the earth's crust, has increased continuously since the first production in 1808. The use of magnesium, and hence the associated research activity, greatly increased during the Second World War because of demand generated by military applications. Recently, the demand for magnesium alloys has again increased rapidly owing to increased efforts by the automotive industry to adopt light materials in order to achieve improved fuel economy and lower emission levels. According to a recent industry review,^[1] there are 60 different types of components, from instrument panels to engine components, in which magnesium is used or is being developed for use, and the use of magnesium in automobile parts is predicted to increase globally at an average rate of 15 pct per year.

Grain size is one of the most important factors determining the quality of cast metal products because it significantly affects the mechanical properties. The grain size of castings can be manipulated by altering various casting parameters, such as the cooling rate, or by adding alloying elements and nucleants (a grain refiner) before or during the casting process. Much work has been performed to achieve control of grain size of most cast metal products, including magnesium alloys. The significant amount of research on magnesium alloys is not because these alloys have a tendency to exhibit coarse grains compared to other cast metals, but because magnesium alloys have the potential to produce much finer grains than do most other alloys.^[2]

Unlike aluminum alloys, where well-established, reliable grain refiners are commercially available, a similar universally reliable grain refiner system does not exist for the range of magnesium alloys. Because of the importance of grain refinement to the development of high-performance magnesium alloys, a study was initiated to improve understanding

of the factors controlling grain refinement. This article presents initial work that has focused on the effect of solute additions. A literature review is also presented that sets the context of the current knowledge of grain refinement in magnesium alloys. Experiments that add to available data on the effect of solute elements on grain size have been conducted and analyzed.

Grain Refinement Methods for Mg Alloys

1. Superheating

This process consists of heating the melt to a temperature well above the melting point for a short time, and then cooling it back to the pouring temperature. The required superheating temperature for successful grain refinement is dependent on the alloy composition, but is commonly accepted to be about 150 °C to 260 °C above the liquidus temperature.^[2] Since successful grain refinement can be obtained by a simple thermal treatment, the influence of impurities and different alloying elements on grain refining efficiency has been intensively investigated,^[2-4] and it has been found that Al (exceeding 1 wt pct), Fe, and Mn are essential elements for maximizing grain refinement by the superheating process, whereas zinc has a negligible effect.^[2,4] Studies by Nelson^[2] and Tiner^[4] showed that Fe and Mn play a significant role for grain refinement by the superheating method.

Other characteristic features of the superheating process include the existence of a specific temperature range for successful grain refinement and fading of the grain refinement when the melt is subsequently held at a low temperature. The use of superheat temperatures on either side of the optimal temperature range for the superheat method can inhibit the grain refining effect, and extended holding times at the pouring temperature after superheating result in grain coarsening and even complete loss of the grain refining effect.^[2,5,6]

Such a large body of work has been conducted to investigate grain refining by superheating that it is difficult to compare all the results. Therefore, only the generally agreed upon characteristics of this method are summarized subsequently.

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- (1) Aluminum is one of the major alloying elements for successful grain refinement, and the degree of the refinement increases and/or the alloy responds to the superheating process more rapidly as the Al content of the alloy increases.^[2,7]
- (2) Binary alloys of Mg with Zn, Ag, Sn, and Cu all respond to superheating. However, binary alloys with Bi, Cr, and Th show no grain refining effect.^[2]
- (3) The degree of grain refinement is suppressed by the presence of elements such as Ti, Zr, and Be even at very low concentration.^[2,4,5,7]
- (4) There are critical minimum contents of both Fe and Mn for successful grain refinement. Also, an excess Mn addition can negate the grain refinement effect.^[2,4]

The mechanism of grain refinement by the superheating treatment is not fully understood. According to Wood,^[8] the solubility of Fe in molten magnesium is very sensitive to temperature, with the solubility of Fe decreasing significantly as temperature decreases. As a result, the excess iron forms insoluble precipitates during cooling of the melt from the superheating temperature, and these may act as nuclei for grains during solidification. The liquid solubility of Fe and Mn in Mg-Al alloys was investigated by Tiner,^[4] and it was found that the solubilities of both elements decrease with increasing Al content. This supports the Fe precipitation hypothesis since the degree of grain refinement obtained by the superheating process increases with increasing Al content.

Hall^[9] suggested that the grain refining effect of superheating may be due to the formation of clouds of magnesium oxide, aluminum oxide, or similar nonmetallic inclusions that act as nuclei during solidification. As the melt temperature increases for the superheating treatment, the possibility of forming such oxides is increased, resulting in a greater number of oxide particles available to act as nuclei or restrict crystal growth during solidification. Whether oxide particles actually do have an effect on grain size has yet to be determined, so this theory remains a possibility. However, the oxide theory fails to explain at least one phenomenon of the superheating process—the existence of the temperature range for successful grain refinement. It may possibly be associated with crystallographic transitions of aluminum oxide with temperature (*i.e.*, $\gamma \rightarrow \theta \rightarrow \alpha\text{Al}_2\text{O}_3$), but this has not been investigated in the literature. However, as pointed out by Nelson^[2] and Tiner,^[4] the possibility of grain refinement by oxides during solidification seems to be limited for the following reasons.

- (1) Significant grain refinement does not result from direct addition of magnesium oxide or aluminum oxide on the surface of the melt or from introduction of oxides by treating the melt with oxygen gas or by addition of proprietary fluxes (such as 310, which contains 15 pct magnesium oxide).^[2,9]
- (2) The grain refining effect can be obtained by superheating treatment in a vacuum and in a closed system isolated from the atmosphere.^[4]
- (3) The effect of Fe and Mn contents on the degree of grain refinement achieved by the superheating process cannot be explained by the oxide theory since small additions of these elements should only have a minor effect on grain nucleation by oxide by changing the surface tension of the melt and thereby affecting the formation of

oxides. However, the grain size is found to be significantly affected by minimal changes in concentration of these elements.

A further theory proposed to explain the phenomenon of grain refining by superheating is the temperature-solubility nucleation theory, which is based on changing particle size corresponding to a change in temperature. Particles that are too large to act as nuclei at normal temperatures may dissolve at higher temperatures during the superheating process and then reform or reprecipitate as finer particles, which are effective nuclei during subsequent cooling.^[2] Coalescence of the particles with longer holding at a lower temperature may explain the deterioration of grain refinement with long holding times at a temperature below the superheating range (such as the pouring temperature). However, this hypothesis fails to explain the existence of the optimal temperature range for the superheating process.

2. Elfinal process

The Elfinal process involves the addition of anhydrous ferric chloride (FeCl_3) into the molten alloy at about 750 °C.^[8] The lower operating temperature compared to that of the superheating method provides some economic advantages and it also allows the melt to be held at the pouring temperature for at least an hour without any loss in grain refinement efficiency.^[2,8] Although this method can produce a grain refining effect similar to that obtained by superheating, it is ineffective in producing grain refinement unless Mn is present^[2] and the alloy also contains more than 3 wt pct Al.^[8] For this reason, Emley^[7] suggested that grain refinement by the Elfinal method involves nucleation by Fe-Mn-Al compounds. Some alloying elements such as Zr and Be interfere with the process, causing grain coarsening.^[10]

3. Carbon additions

Although the superheating and Elfinal methods produce satisfactory grain refinement for Mg-Al alloys, the problems associated with these methods prompted the development of the carbon inoculation method. This process involves the introduction of carbon into the melt in various ways, including addition of paraffin wax, lampblack, some organic compounds such as hexachloroethane and hexachlorobenzene, and bubbling the melt with carbonaceous gases.^[2,5,7] Carbon addition methods have become the major industrial grain refinement technique for Mg alloys because they offer some important practical advantages such as lower operating temperature, large melt volumes, and less fading with long holding time.

The effect of common alloying elements such as Al, Zn, and Mn on grain refinement by carbon addition was investigated, and it was found that at least 0.5 wt pct of Al is necessary before grain refinement can be achieved.^[11] For this reason, aluminum carbide (Al_4C_3) or a combination of $\text{Al}_4\text{C}_3 \cdot \text{AlN}$ particles, which form during the carbon treatment, is regarded as the major nucleating phase.^[5,7] As well as forming the proposed nucleants, the addition of Al may also promote nucleation by generating a solute diffusion layer during growth that can provide constitutional undercooling. However, some alloying elements such as Zr, Be, Ti and some rare earth elements interfere with the method as they do in the superheating process.^[2,11] These elements probably form much more stable carbides than aluminum carbide, and grain coarsening occurs unless these new carbides are good nucleants for Mg. Settling of the carbides

formed is another possible explanation of the reduction in grain refinement.

Introduction of carbon into the melt can be achieved by bubbling with carbonaceous gas. The effect on grain size of carbonaceous gas treatment has been well summarized in early studies,^[2,5,7] and it has been found that gases such as carbon dioxide, acetylene, and natural gas all produce grain refinement equivalent to that obtained by superheating. However, it was also found that the grain refinement obtained with carbonaceous gas is sometimes reduced or lost upon remelting or holding the melt at a low temperature, just as for grain refinement by superheating.^[5]

The addition of various solid carbon containing materials such as granulated graphite or granulated aluminum carbide produces grain refinement, although there are instances in which the results obtained are somewhat erratic, probably because of difficulties in dissolving or dispersing the particles or granules.^[5] Recent studies of the effect of SiC particle additions on grain size of AZ91 (9 pct Al and 0.8 pct Zn) alloy showed that significant grain refinement results, even with additions of small amounts of SiC particles (0.5 vol pct, average particle diameter 7 μm).^[12] A number of SiC particles were found within the primary Mg grains, suggesting a possible heterogeneous nucleation mechanism for grain refinement. This is supported by a favorable crystallographic orientation relationship between the (111) plane of SiC and the (0001) plane of Mg with a relatively small lattice registry (4 pct).^[12] Luo^[12] also found that some of the SiC particles were pushed out to the grain boundaries, and proposed that the grain refinement effect of SiC may also be attributed to a reduction of the growth rate in the primary phase.

Since carbon is a major component of organic materials, some organic compounds have been used as grain refining agents in magnesium. It has been found that carbon can be most advantageously added to the melt by the use of an organic chloride.^[5] The most commonly used chlorides are carbon hexachloride (C_2Cl_6) and carbon tetrachloride (CCl_4). Since carbon hexachloride is very effective and enables both degassing and grain refining at the same time, it has been used widely for commercial grain refinement of Mg-Al alloys.^[13] However, the emission of toxic gases such as chlorinated hydrocarbons results in environmental problems, and the requirement for relatively high temperatures for an enhanced grain refining effect has led to the development of a different type of carbon-based grain refiner. Research conducted by Karlsen *et al.*^[13] showed that a mixture of wax-fluorspar-carbon is a more effective grain refiner for Mg-Al alloys than hexachloroethane without any of its environmental concerns.

4. Agitation method

The agitation method simply involves stirring the melt vigorously prior to casting and is relatively successful when conducted at relatively high temperatures. The exact operating temperature for grain refinement has not been determined, but Hultgren and Mitchell^[14] observed that slow stirring by a large stirrer at lower temperatures (below 760 $^\circ\text{C}$) may produce grain coarsening rather than refining. According to Hultgren's observations of successful grain refinement of ASTM No. 17 alloy (9 pct Al, 2 pct Zn, and 0.3 pct Mn) by the agitation method, the average grain size obtained was approximately equivalent to that obtained with

superheating. In order to improve the grain refining effect of agitation, a combination of carbonaceous treatment and severe local agitation can be employed.^[2] A similar result was reported by Tiner,^[4] who found that stirring at the superheating temperature improved the degree of grain refinement achieved by the superheating method. Experimental data and publications about the agitation method are limited and the mechanism of this process is not clear. Nelson^[2] suggested that agitation merely speeds up an unfavorable coalescence of nuclei at low temperatures, which leads to grain coarsening. At higher temperature, on the other hand, agitation increases the rate of solution or transformation of the nuclei forming phase, resulting in grain refinement.

5. Grain refinement by Zr additions

Zirconium can be added to pure magnesium or Mg alloys containing Zn, Ag, Y, or Th^[10] for grain refinement. One of the major benefits derived from the zirconium additions is the superior efficiency of grain refinement compared to other methods. The mechanism of grain refinement by Zr in magnesium is not clear, but the most commonly accepted hypothesis relates to the lattice registry between Zr and Mg. Zirconium has the same hcp crystal structure as magnesium, and the lattice parameters of Zr ($a = 0.323$ nm, and $c = 0.514$ nm) are very close to those of Mg ($a = 0.320$ nm, and $c = 0.520$). It is believed that Zr particles, elemental or intermetallic, may be a powerful nucleant of magnesium because of this similarity in the lattice parameters, therefore providing efficient nucleation.

As a peritectic reaction occurs between Mg and Zr at 654 $^\circ\text{C}$, the possibility of a peritectic reaction mechanism has been proposed for the grain refinement.^[7] However, according to the Mg-Zr phase diagram, the peritectic reaction occurs when the Zr content exceeds about 0.58 wt pct. Since significant grain refinement is produced at lower concentrations than this, nucleation by undissolved particles of zirconium or compounds of Zr with other elements must be considered a possibility. The degree of grain refinement obtained by the addition of zirconium is much more efficient compared to that of the other grain refinement methods described previously and the process itself is simple. However, one major problem with this method is the limited choice of alloy systems to which it can be applied since some alloying elements, particularly Al, interfere with the process.^[7]

In spite of this problem, Zr addition is the most commonly used grain refinement method for alloys such as Mg-Zn or Mg-Zn-Y. It has recently been reported that a combined addition of Ca and Zr produces a stronger grain refining effect than zirconium alone.^[15]

6. Grain refinement by Sr additions

Recently, strontium has been reported an effective grain refiner of Mg-Al alloys.^[16,17] Gruzleski and Aliravci^[17] reported that a strontium level in the range of 0.005 to 0.03 wt pct, added to a melt of AZ91 alloy, had the notable effect of reducing the grain size as well as microporosity (grain size reduced from 225 μm to 75 to 150 μm). In their study, the base materials had already been refined by carbon additions, but the addition of strontium produced further significant grain refinement.

Similar results have been reported by Nussbaum *et al.*^[16] In their experiments, addition of strontium to an AZ91E alloy produced significant grain refinement, and they found

that a moderate amount of needle-shaped Al_4Sr and Mg_2Sr precipitates formed when the amount of Sr used increased. Furthermore, at high Sr contents (more than 3 wt pct), strontium forms highly stable, relatively coarse precipitates with Al and Mg. As it has not yet been determined whether these precipitates are suitable nucleation sites, the possibility of nucleation by these particles cannot be excluded.

The mechanism of grain refinement by strontium has not been identified. However, the effect of Sr on growth kinetics can be understood by the growth restriction effect of Sr rejected ahead of the solid/liquid interface. Because its solid solubility in magnesium is relatively small (~ 0.11 wt pct), rapid enrichment of solute in the liquid ahead of the growing interface would be expected during solidification. Gruzleski and Aliravci^[17] proposed that Sr may poison the grain surface or poison the fast growing directions of the grains by preferential adsorption of Sr at these sites. The possibility of changing the liquid surface tension has also been suggested by the same authors.

7. Summary

Several grain refinement methods have been developed for Mg alloys, but there is no clear understanding of their mechanisms. This lack of understanding of the mechanism of grain refinement in Mg alloys creates some confusion and leads the industry to rely on empirical approaches for grain refinement. To date, research into grain refinement of magnesium alloys has mainly been focused on enhancing nucleation by the addition of nucleant particles, and the role of solute on the rate of nucleation, and hence grain refinement, has been recognized only relatively recently.^[18,19] The grain refinement methods discussed previously, together with their proposed mechanisms (nucleant particle and/or solute effect), are summarized in Table I.

II. EXPERIMENTAL

Magnesium alloys were prepared in an electrical resistance furnace using commercial purity (99.7 pct) Mg and Al ingots. Commercial AZ91D alloy supplied by Norsk Hydro was also used. The melting process was conducted in mild steel crucibles under a protective atmosphere of 0.5 pct SF_6 in air. The contact time was about 15 minutes at 700 °C and 5 minutes prior to pouring the melt was stirred for 30 seconds. The melt was poured into a mild steel mold preheated to 200 °C. The mold consisted of a cubic block with 100-mm sides, incorporating a cylindrical cavity of 25-mm radius and 70-mm depth (actual sample size).

The effect on grain size of additions of commercially

available alloying elements or master alloys was investigated. Two different types of Sr-Al master alloys were used. A 90 wt pct Al–10 wt pct Sr master alloy rod was used for low Sr additions (0.01 and 0.1 wt pct Sr), while a 90 wt pct Sr–10 wt pct Al master alloy supplied by Timminco Pty Ltd. was used for higher Sr addition levels (>0.1 wt pct). A Mg-Zr master alloy containing 33 pct Zr, supplied by Magnesium Elektron Ltd., was used for Zr additions, while the Si and Ca additions were made using commercially available Si chips and granular Ca.

Each sample was sectioned vertically or transversally in half and subjected to solution heat treatment in an air furnace to reveal the grain boundaries. The samples were held in the furnace for 30 minutes at 413 °C, then air-cooled. Alloys containing less than 5 wt pct Al were etched with acetic-picric acid (10 mL acetic acid, 4.2 g picric acid, 10 mL H_2O , and 70 mL ethanol), and alloys containing more than 5 wt pct Al were etched with citric acid (5 g citric acid and 95 mL H_2O). Etching was performed at room temperature for 2 to 3 seconds.

Owing to different cooling rates between the center and edge of the samples, optical micrographs were taken for grain size measurement from each of three different sections (edge, one-half radius, and center) of each sample. Grain size measurements were performed using the linear intercept method described in ASTM standard E 112-88, and more than 50 intercepts were counted for each grain size determination. Chemical analysis was conducted by the Inductively Coupled Plasma Spectroscopy (ICP-AES) method.

III. RESULTS

A. Effect of Al on Grain Size

As mentioned in the experimental procedure, the grain size was measured in three different regions of the sample since there was significant variation in grain size from the center to the edge of the casting as a result of differences in the cooling rate. Pure Mg had long columnar grains growing from the wall and reliable measurements of grain size could not be made. In this case, grain size was measured as the width of the columnar grains. The effect of Al additions on grain size is shown in Figure 1. The addition of Al caused significant grain refinement. Adding small amounts of Al (1 and 3 wt pct) produced a transition to equiaxed grains and a significant reduction in grain size. This effect continued up to about 5 wt pct Al. Increasing the Al content above 5 wt pct did not produce any further significant refinement of the grain size. The grain size of AZ91 was comparable to that

Table I. Summary of Grain Refinement Methods for Different Magnesium Alloys

Alloys	Methods	Proposed Mechanism	Reference
Mg	Al, Zn, RE, Th, Si, Zr addition	growth restriction by solute effect and/or nucleant particles	2, 12
Mg-Al(-Zn-Mn)	C inoculation	nucleation by Al_4C_3 , AlN	2, 13
	superheating	nucleation by Fe compounds	2, 7
	Sr addition	growth restriction	19, 20
	agitation	redistribution of nucleants	16
	SiC addition	nucleation by SiC particles and/or restriction of growth	14
Mg-Al-Mn(-Zn)	Elfinal process	nucleation by Fe-Mn-Al compounds	2, 12
Mg-Zn(-RE-Mn)	Elfinal process	nucleation by Fe compounds	2, 12
	Zr addition	nucleation by Zr particles	
Mg-Y(-Zn)	Ca + Zr	growth restriction/nucleation by Zr particles	18

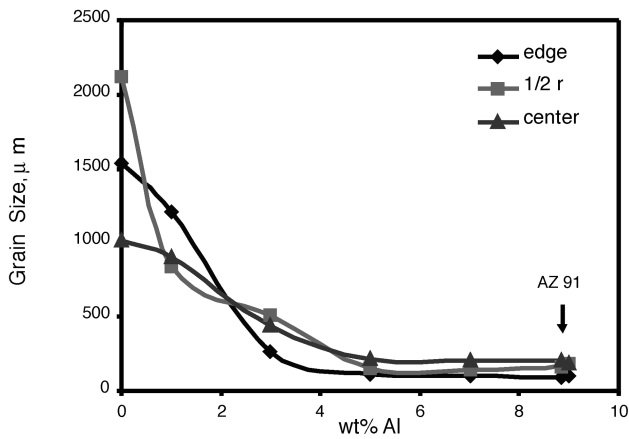


Fig. 1—Grain size behavior as a function of Al concentration.

of the Mg-9Al binary alloy. At low Al contents, below 3 wt pct, the variation in grain size in the different sections of the sample (edge, one-half radius, and center) was much greater than that found at higher Al contents. Another effect of Al on microstructure was a reduction of the length of columnar grains. While pure Mg had long columnar grains growing from the edge toward the center, an addition of 3 wt pct Al suppressed the columnar growth by about 75 pct and also produced much narrower columnar grains. The columnar structure was not present once the Al concentration exceeded 5 wt pct. The reduction of grain size and columnar grains with increasing Al concentration is clearly seen in Figure 2.

B. Effect of Sr on Grain Size

The effect of strontium additions on grain size was investigated in low (3 wt pct) and high (9 wt pct) Al-containing binary magnesium alloys using Sr levels ranging from 0.01 to 1 wt pct (Figure 3). For the low Al content alloy (Figure 3(a)), the effect of Sr addition on grain size showed a similar pattern to that observed with Al additions (*i.e.*, large change in grain size with initial Sr additions and a small change upon further additions). The addition of 0.01 wt pct Sr had a dramatic grain refining effect in the Mg-3Al alloy. However, a further addition of Sr to 0.1 wt pct caused an increase in grain size, or at least did not show any further significant

grain refinement. At this stage, the grain size was still smaller than that of the unrefined alloy, although larger than for the alloy refined by 0.01 wt pct Sr. A further addition of Sr to 0.3 wt pct resulted in a decrease in grain size, and this trend continued with increased Sr contents up to 1 wt pct.

The effect of strontium on grain size in Mg-9 wt pct Al binary alloy (Figure 3(b)) showed a somewhat different trend to that in the Mg-3Al alloy described previously. Fluctuations in grain size with different levels of Sr additions were observed. There was an increase in grain size after addition of 0.01 and 0.1 wt pct Sr, followed with slight reductions in grain size upon further additions of Sr until 1 wt pct Sr was added. The extent of change in grain size over this range of Sr additions was within experimental error, and the alloy refined with 1 wt pct Sr compared with that of the nonrefined Mg-9Al binary alloy; there is no significant difference in grain size.

Further experiments were performed to investigate the effect of strontium additions in low Al-containing alloys (pure Mg and Mg-1 wt pct Al with 0.3 wt pct Sr addition). The results shown in Figure 4 indicate that Sr had quite a strong grain refining effect in both samples, but the effect was more pronounced in pure Mg than in the Mg-1Al alloy. Addition of 0.3 wt pct Sr to pure Mg suppressed most of the columnar structure. The length of columnar grains decreased from 23 to 10 mm, and the columnar grains were much finer than those in unrefined pure Mg. In the Mg-1Al alloy, the length of columnar grains decreased slightly, from 10 to 7 mm; however, the width of the columnar grains did not change significantly. Furthermore, the average grain size of the Mg-1Al-0.3Sr sample was larger than in the Mg-0.3Sr alloy. This is clearly depicted in the macrographs of the Mg-0.3Sr and Mg-1Al-0.3Sr samples shown in Figure 4(b).

C. Effect of Si on Grain Size

As silicon is a commonly used alloying element in magnesium alloys, it is of interest to determine its effect on grain size. Alloys with a range of Si levels were produced by the addition of Si to pure magnesium. During these experiments, a problem was encountered with dissolving the Si chips. Each melt was held at 700 °C for 2 hours with constant stirring to dissolve the Si completely; however, the chemical analysis showed that the silicon concentration of the final alloys was far below (almost half) the expected composition.

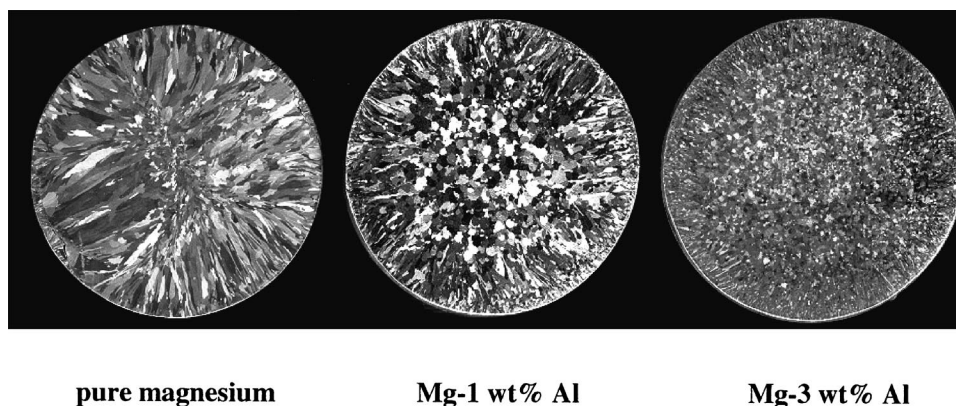


Fig. 2—Macrographs of pure Mg and Mg-Al alloys with 1 and 3 wt pct of Al. The grain size of samples with more than 5 wt pct Al is too small to be revealed macroscopically. (Note that the diameter of the samples is 50 mm.)

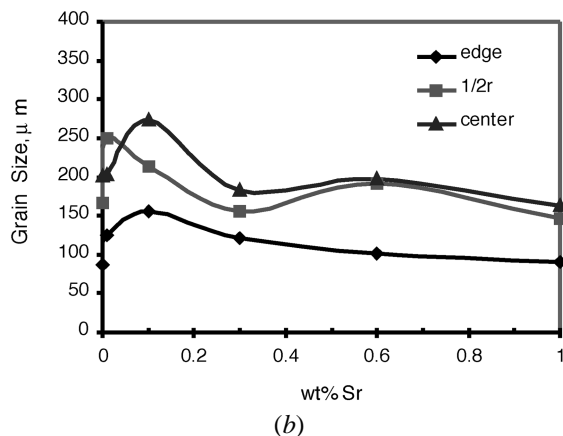
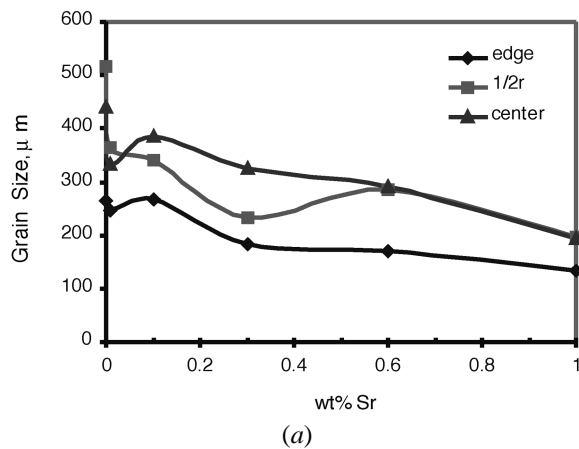


Fig. 3—Grain size of (a) Mg-3Al binary alloy and (b) Mg-9Al binary alloy with different levels of Sr addition (note that the grain size of Mg-9Al binary alloy is far smaller than that of Mg-3Al binary alloy, and the graphs employ different scales).

The grain size results are shown in Figure 5. From this figure, it can be seen that a small addition of silicon produced a strong grain refining effect in pure magnesium, indicating that silicon is an effective grain refiner for magnesium. After a small addition of Si (0.07 wt pct), long columnar grains were still present. However, when the silicon level was increased to 0.15 wt pct, the columnar grains were suppressed and fine equiaxed grains were formed throughout the sample. The grain size at the edge of the samples remained constant with further additions. Micrographs of these samples are shown in Figure 5(b), and the decrease in grain size with increased silicon content is clearly observed.

D. Effect of Zr on Grain Size

Micrographs showing the effect of zirconium additions on the grain size of pure magnesium are presented in Figure 6. The Zr concentration was planned to vary from 0.1 to 1 wt pct; however, chemical analysis results showed consistently lower Zr concentrations. As expected, the addition of Zr produced extremely fine-equiaxed grains with a distinct hexagonal shape. Unlike for the other elemental additions, grain size measurement was performed only at the center of each sample. This was because relatively large variations in grain size (e.g., pockets of small equiaxed grains surrounded by large columnar grains) within the different sections of each

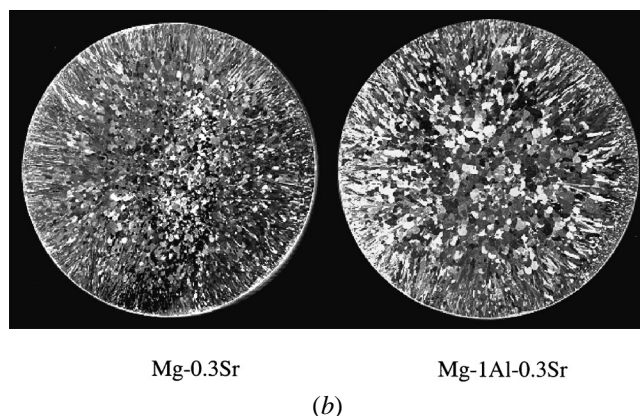
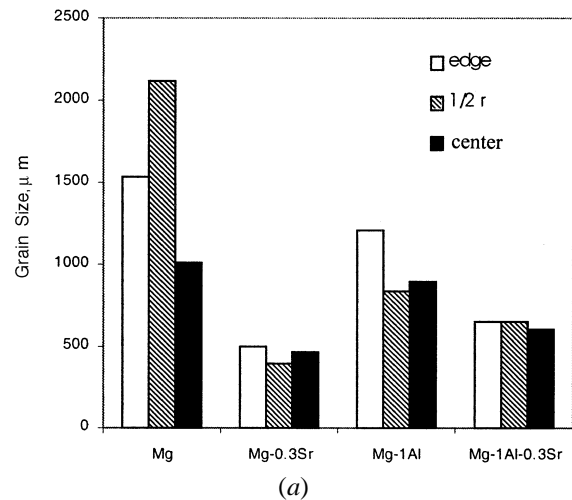
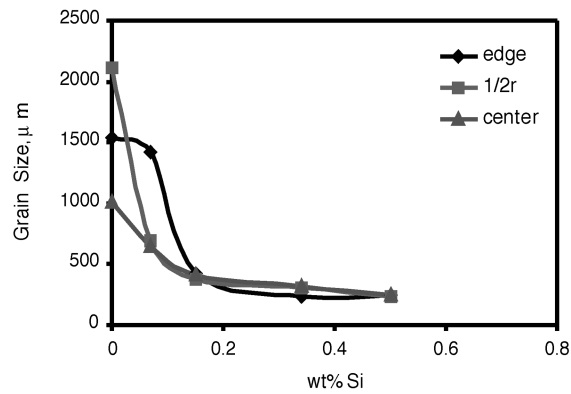


Fig. 4—(a) Grain size of pure Mg and Mg-1Al binary alloy with 0.3 wt pct Sr addition (the grain size of unrefined pure Mg and Mg-1Al alloy is shown for comparison), and (b) micrographs of Mg and Mg-1Al binary alloy grain refined with 0.3 wt pct Sr. The grain size difference between Mg-0.3Sr and Mg-1Al-0.3Sr is observable. (Note that the diameter of the samples is 50 mm.)

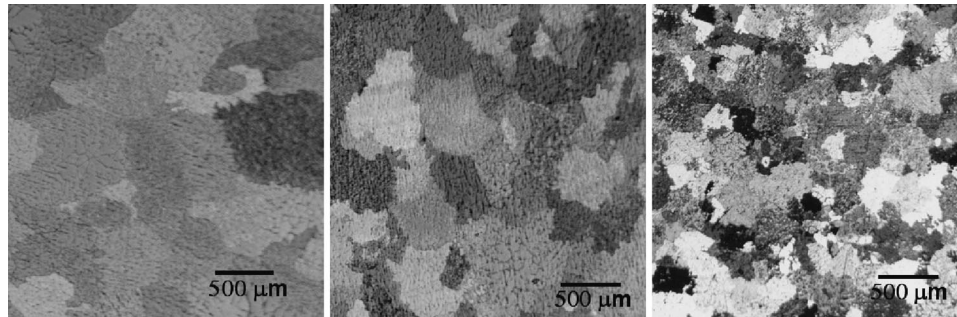
sample were observed, especially in low Zr content samples (0.04 and 0.15 wt pct Zr). The trend in grain size with addition level was very similar to that observed with Al and Si additions. Initially, as the Zr content increased, grain size decreased rapidly (up to 0.04 wt pct). Further additions of Zr (up to 0.15 wt pct Zr) resulted in a more gradual reduction in grain size. However, when the Zr level was increased to about 0.32 wt pct, the magnitude of the grain size reduction was minor and the grain size seemed to be reaching the saturation level (Figure 6(a)). Even though the grain size behavior with Zr additions was quite similar to that of Si additions, there was a significant difference in the actual grain size that was observed at the saturation point. In the case of Si additions, the minimum grain size at the stabilization level was approximately 240 μm while it was approximately 108 μm with Zr additions. Micrographs showing the effect of Zr on grain size are shown in Figure 6(b).

E. Effect of Ca on Grain Size

Significant grain size reductions in pure magnesium were observed with Ca additions. As can be seen in Figure 7, the grain size with increased Ca level showed a similar trend



(a)



Mg-0.07 wt% Si

Mg-0.15 wt% Si

Mg-0.5 wt% Si

(b)

Fig. 5—(a) Grain size of pure Mg with a range of Si concentrations, showing a dramatic decrease in grain size with the initial addition of Si and stabilization after 0.15 wt pct Si addition—a typical solute effect on grain size, and (b) micrographs of the samples.

to that of other elements (*e.g.*, a large reduction in grain size with initial additions, a relatively minor effect on grain size with subsequent additions, followed by stabilization of grain size). The grain size seemed to reach a saturation level after the addition of 0.4 wt pct Ca, and further additions had only a minor effect on grain size. The actual grain size at the saturation level was around 270 μm , which is similar to that achieved with Si additions (240 μm).

IV. DISCUSSION

Grain refinement in commercial practice usually involves the addition of foreign nucleants and/or alloying elements into a melt before casting. The choice of effective nucleating agents and alloying elements mostly depends on the alloy being refined, and the resultant grain size varies depending on the type and amount of inoculants or alloying elements added. The effect of solute elements on grain size is as important as that of nucleant particles, since solute elements play a significant role in controlling the growth of the nucleated grains and in subsequent nucleation.^[20,21] The effect has been investigated in various Al alloy systems^[18,19,22] and explained in terms of the growth restriction factor (GRF). Addition of solute elements generates constitutional undercooling in a diffusion layer ahead of the advancing solid/liquid interface, which restricts grain growth since the diffusion of the solute occurs slowly, thus limiting the rate of crystal growth. In addition, further nucleation occurs in front

of the interface (in the diffusion layer) because nucleants in the melt are more likely to survive and be activated in the constitutionally undercooled zone (constitutional undercooling is a major driving force for nucleation).

The GRF can be calculated using binary phase diagrams. The GRF equals $\sum_i m_i C_{o,i} (k_i - 1)$, where m_i is the slope of the liquidus line (assumed to be a straight line), k_i is the distribution coefficient, and $C_{o,i}$ is the initial concentration of element i . It should be noted that this equation is only applicable for alloying elements present in dilute concentration levels. The GRF values for various alloying elements in magnesium alloys have been determined using binary phase diagrams and are shown in Table II. The GRF values of Zr, Ca, and Si are relatively large compared to those of other elements such as Al, Y, Sn, *etc.*, indicating more powerful growth restriction, and hence stronger grain refining ability with small addition levels of these elements. The Zr has the highest growth restriction factor value among the common alloying elements, indicating significant grain refinement potential associated with its strong segregating power.

An interesting result was observed for Zr additions because the powerful grain refining effect of Zr is generally believed to be produced by peritectic zirconium particles. However, the results of chemical analyses showed that the maximum zirconium concentration achieved in the experimental samples was 0.32 wt pct, which is far below the

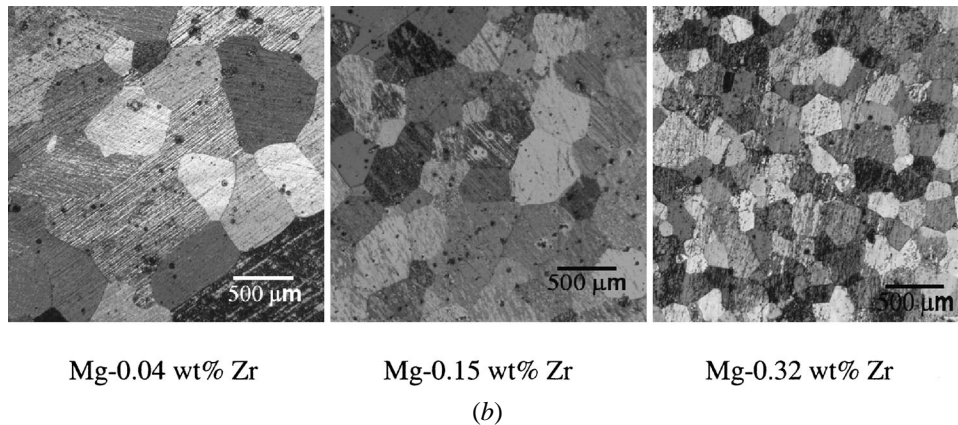
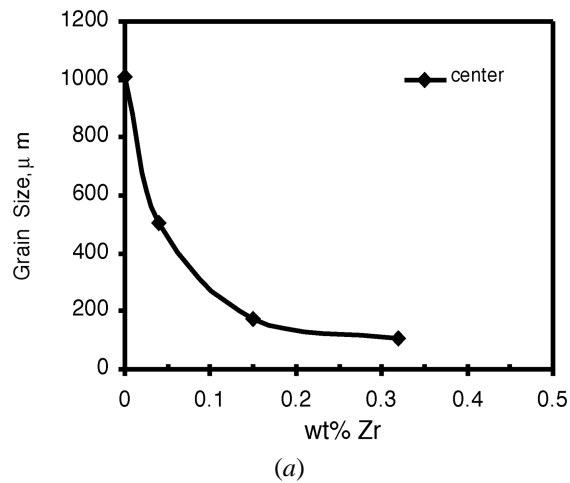


Fig. 6—(a) Grain size of pure Mg with various levels of Zr addition (the grain size measurement was made only at the center of the samples), and (b) micrographs of samples with Zr additions showing dramatic decreases in grain size.

peritectic point (0.56 wt pct). In this case, it seems unlikely that zirconium is present in the form of nucleant particles, so the grain refinement achieved by the addition of zirconium may instead be caused by the high growth restriction.

Figure 8 depicts the relationship between grain size and GRF value for all the elements studied in the current work. Grain size is plotted against GRF values calculated using the measured concentrations of each alloying element. From the concept of the GRF, the effect of solute elements on grain size should be a function of the GRF value, and therefore independent of the alloy system in question. In other words, under the same casting conditions, a similar grain size is expected from samples with similar GRF values, regardless of alloying elements, if the nucleant particle population is the same. However, as can be seen in Figure 8, there is a reasonable degree of variation in grain size among samples with different alloying element additions at a given GRF value. This is especially apparent at GRF values up to 10, with Zr, Si, and Ca producing somewhat similar grain sizes, with that achieved with Al additions being significantly larger. These variations could be generated by unknown nucleant particles that may be introduced into the melt with the solute additions, or by any reactions that may occur between those alloying elements and magnesium. Also, the differences in the number of crystals nucleated on the mould wall that survive during the casting process may contribute

to the observed variations. Such differences in the number of wall crystals could occur because the melt superheat changes with the solute additions. This will be more significant with Al addition since the addition level is much higher than with other elements and the depression of liquidus temperature therefore more significant.

The effect of such nucleant particles is also suggested by the shift in GRF value at which the saturation level is reached. For additions of aluminum, the saturation level is reached at a GRF value between 20 and 30, however, while the saturation level is reached at much lower GRF values for the other elements. It is difficult to exactly determine the composition where the saturation level would be reached for Si additions because of experimental difficulties, but it appears that it would be reached by a GRF value around 10, similar to that of the Ca and Zr additions. This shift in saturation point may be caused by enhanced nucleation as a result of the presence of introduced nucleant particles. As mentioned previously, the lattice parameters of Zr are quite similar to those of Mg, and if any undissolved Zr particles exist, they may act as nucleants, helping to generate finer grains even below the peritectic composition.

The experimental results show a minimal reduction in grain size with further additions of alloying elements after the saturation level is reached. It is therefore reasonable to assume that addition of zirconium to reach a GRF value

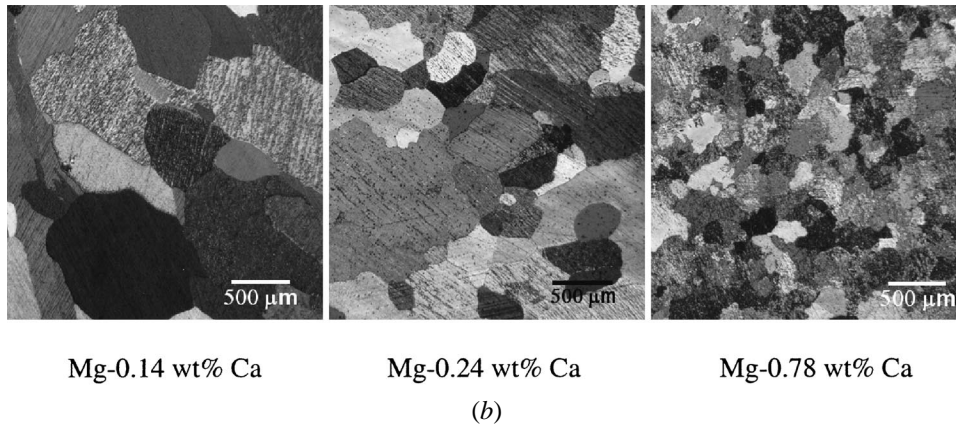
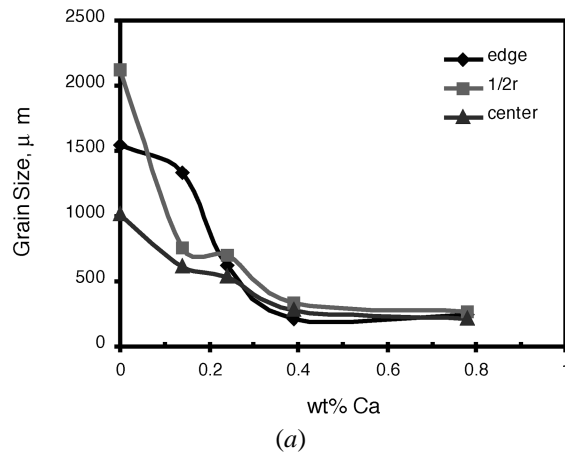


Fig. 7—(a) Grain size of pure Mg with various levels of Ca addition, and (b) micrographs of samples with Ca additions.

Table II. Slope of the Liquidus Line (m), Equilibrium Distribution Coefficient (k), and Growth Restriction Parameter $m(k - 1)$ for Various Alloying Elements in Magnesium

Element	m	k	$m(k - 1)$	System
Zr	6.90	6.55	38.29	peritectic
Ca	-12.67	0.06	11.94	eutectic
Si	-9.25	≈ 0.00	9.25	eutectic
Ni	-6.13	≈ 0.00	6.13	eutectic
Zn	-6.04	0.12	5.31	eutectic
Cu	-5.37	0.02	5.28	eutectic
Ge	-4.41	≈ 0.00	4.41	eutectic
Al	-6.87	0.37	4.32	eutectic
Sc	4.02	1.99	3.96	peritectic
Sr	-3.53	0.006	3.51	eutectic
Ce	-2.86	0.04	2.74	eutectic
Yb	-3.07	0.17	2.53	eutectic
Y	-3.40	0.50	1.70	eutectic
Sn	-2.41	0.39	1.47	eutectic
Pb	-2.75	0.62	1.03	eutectic

around 30 would have only a very small effect on grain size. Thus, the grain size with zirconium addition at this GRF value would be about $100 \mu\text{m}$, while with aluminum addition, it is about $200 \mu\text{m}$. Considering a cube-root relationship between grain volume and grain size measurement, there must be about 8 times as many nucleant particles activated in

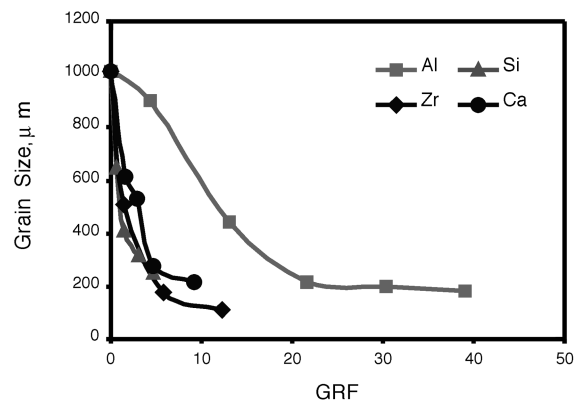


Fig. 8—Grain size of pure magnesium for a range of different alloying elements as a function of GRF value.

the zirconium sample compared with the aluminum sample. Since only a small proportion of nucleants present in a melt is activated, the difference in the actual number of nucleants present in the zirconium and aluminum samples must be enormous.

The formation of any intermetallic compounds with the alloying elements or other impurities may also contribute to nucleation if those particles are powerful nucleants and form before the primary phase. From the results of many

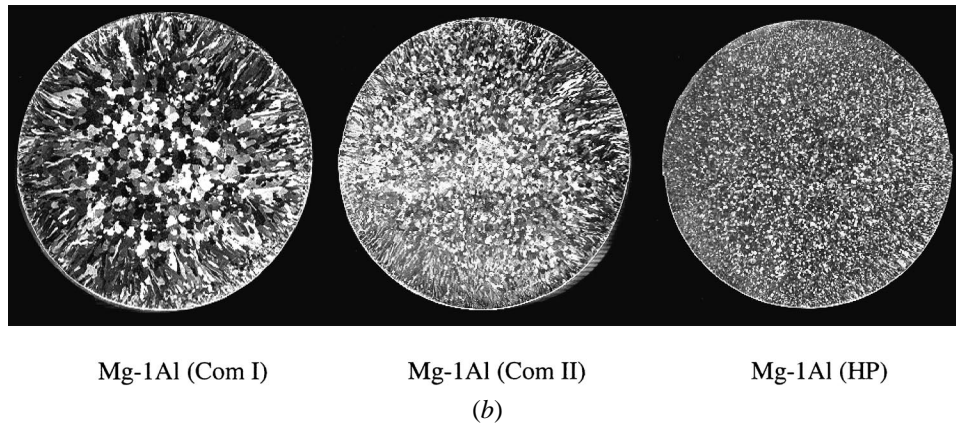
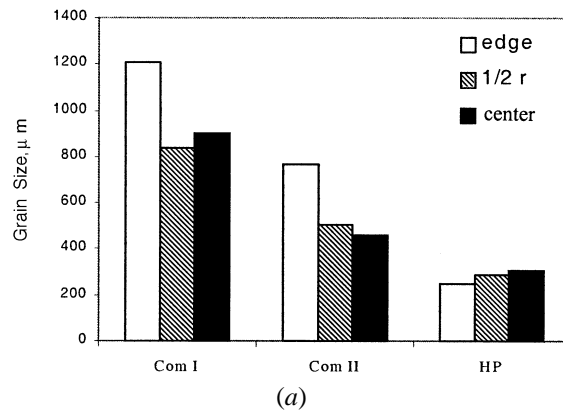


Fig. 9—(a) Grain size of Mg-1Al alloys made from three ingots with different purity levels (99.7 and 99.98 pct). Com I and Com II samples were made using two different commercial purity ingots (99.7 pct), while the HP sample was cast using a high-purity ingot (99.98 pct). (b) Macrographs of the samples. The difference in grain size is clearly visible. (Note that the diameter of the samples is 50 mm.)

previous studies,^[5,7,8] Fe-Al-(Mn) intermetallic compounds are believed to be powerful nucleants in various Mg-Al alloys. In contrast, as mentioned previously, some Zr intermetallic compounds with aluminum or some rare earth elements seem to have an adverse effect on nucleation of magnesium since grain refinement produced by the addition of zirconium disappears when these alloying elements are also present. An example of the effect of such particles on grain size is shown in Figure 9. The composition of all three samples was around Mg-1 wt pct Al (confirmed by chemical analysis) and casting conditions were kept constant during sampling. The only difference was the base ingots used. The sample with the finest grains was cast using a 99.98 pct purity Mg ingot, while the others were cast from commercial purity (99.7 pct) ingots from different batches. The maximum difference in grain size among these samples is more than 500 μm and the difference is clearly visible in the macrographs shown in Figure 9(b). Obviously, the number of nucleant particles present in the melt and/or their potency is substantially different in the three base ingots. Whether this is due to certain intermetallic compounds or other unknown particles is uncertain, but the effect of impurities on changing the number of nucleation events needs to be considered.

The effect of impurity (Fe, Mn) level on grain size during the superheating process was investigated by Nelson^[2] and Tiner.^[4] It was found that the resultant grain size after grain refinement was affected significantly by the amount of Fe

and Mn present, with a finer grain size in the higher purity sample, which is similar to the results of the present study. However, if the Fe and Mn precipitates were powerful nucleants, smaller grains would be expected when the base material contained more of these elements. Therefore, the possibility of nucleant poisoning by the Fe-Mn phase remains, so the formation of compounds of Fe and/or Mn with other elements may cause grain coarsening rather than grain refining, as proposed by Nelson.^[2] If certain unknown nucleants exist in Mg or Mg-Al alloys that readily combine with other trace elements to form new precipitates, then an increase in the level of such impurities would cause more of the nucleants to be incorporated. If these new compounds are not powerful nucleants at the normal casting temperature, the nucleation potency would be reduced and grain coarsening would result. As the most common trace elements in magnesium, Fe and Mn are more likely than others to be involved in poisoning the unknown nucleants, and this assumption is supported by the results of the chemical analyses of the commercial purity and high-purity ingots shown in Table III. Of all impurities tested, appreciable differences in concentration were detected only for Fe and Mn, so it seems possible that the increase in concentration of these elements is related to the observed increase in grain size.

Poisoning of nucleants may occur during the addition of strontium to Mg-Al alloys. As observed in Figure 4, the addition of strontium to pure magnesium produces a pronounced grain refinement even though the GRF value is

Table III. Chemical Analysis Results of the Three Mg-1Al Alloys Produced from Different Base Ingots

Sample	Element							
	Mg	Al	Be	Cu	Sr	Fe	Mn	
Mg-1Al 99.7 pct purity mg ingot I	bal	1.16	<0.001	<0.005	<0.001	0.02	0.02	
Mg-1Al 99.7 pct purity mg ingot II	bal	1.03	<0.001	<0.005	<0.001	0.02	0.01	
Mg-1Al 99.98 pct purity mg ingot	bal	1.14	<0.001	<0.005	<0.001	<0.01	<0.01	

small. This may indicate the presence of nucleants formed by a reaction between Mg and Sr. As the concentration of Al increases, the formation of Al₄Sr would become more favored, and the grain refining effect decreases or vanishes. Nussbaum *et al.*^[16] reported the presence of a large proportion of Al₄Sr relative to other precipitates in AZ91E alloy with 1 wt pct Sr addition. However, they also reported significant grain size reduction with Sr addition in contrast to the results obtained in the present study. Grain refinement with Sr addition was also reported by Gruzleski and Aliravci.^[17] These seemingly contradictory results may occur because of the different nucleation behavior of the base materials used. The base material used by Gruzleski and Aliravci had been grain refined by carbon inoculation prior to Sr addition. If, as they proposed, Sr restricts grain growth by forming adsorptive Sr films and so providing sufficient time for more carbon substrates to be activated, grain refinement could be obtained. Nussbaum *et al.* did not use pre-grain-refined material, but AZ91E, which is a high-purity alloy, particularly low in Fe and Mn. The proposed hypothesis with poisoning of nucleants with Fe and/or Mn in the alloy may form a basis for explaining the difference between these results and the results of the current work. In AZ91E, the nucleant particles could remain in their original form because of the low Fe and Mn levels, and nucleation could be enhanced by the addition of Sr through growth restriction. In contrast, commercial purity Mg and Al ingots were used to make the Mg-9Al binary alloy in the present work, and the nucleant particles in this alloy may therefore have been poisoned by the Fe and/or Mn. It would be of interest to investigate these aspects of grain refinement of Mg alloys further.

V. CONCLUSIONS

1. The addition of certain solute elements to magnesium leads to a decrease in grain size. Small additions have the greatest effect with the grain size reaching a relatively constant value at higher levels.
2. The addition of aluminum produces some grain refinement, mainly because of the growth restriction effect caused by increased constitutional undercooling.
3. The addition of strontium produces significant grain refinement in low aluminum content alloys, and particularly in pure magnesium. The addition of strontium to a binary Mg-9Al alloy does not produce grain refinement, or rather the grain refining effect is negligible. The effect of strontium seems to be caused by both growth restriction effects and the introduction of nucleant particles. Poisoning of the nucleant particles may occur with addition of aluminum.

4. The addition of a small amount of zirconium, calcium, or silicon produces a strong grain refining effect in pure magnesium. The trend of grain size variation with additions of these elements is similar to that of aluminum, although the composition range over which these elements produce grain refining is different for each element.
5. Aluminum, zirconium, calcium, and silicon produce grain refining at different concentrations because of their different segregating power, and the grain size produced is different at equal GRF values. This difference is most likely due to the introduction or formation of nucleating particles with the additions.
6. Considerable variation in grain size was detected with different base materials, and this variation seems to be related to impurity level. The higher the purity level, the finer is the resultant grain size. It is proposed that Fe and Mn present in magnesium can significantly affect grain refinement efficiency.

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