GRAIN REFINEMENT OF AZ91E AND Mg-9 WT.% Al BINARY ALLOYS USING ZINC OXIDE

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Abstract

For enhanced fuel economy lightweight components are essential in automotive design. Being the lightest structural metal, Mg alloys are potential lightweight candidates. However, due to insufficient strength, Mg alloys are not being used extensively in the automotive industry. Grain refinement is a proven method to increase strength. In this research, the influence of ZnO on the grain size of AZ91E and Mg-9 wt.% Al binary alloy was investigated. With an addition of 0.75 wt.% ZnO, the average grain size of the AZ alloy decreased from 217 µm to 108 µm. For the binary alloy, the grain size reduced from 288 µm to 93 µm with an addition of 3 wt.% ZnO. No significant fading of ZnO grain refiner was observed for both the alloys. The grain refinement was attributed to ZnO particles providing heterogeneous nuclei, and grain growth restriction due to Zn solute, which was liberated from ZnO.

Keywords: *grain refinement, magnesium, AZ91E, Mg9 wt.% Al, ZnO*

Introduction

The demand for reduced carbon emissions and increased fuel economies has provided stimulus for new lightweight materials to be used in automotive and aerospace applications. Magnesium (Mg), 85% lighter than iron and 35% lighter than aluminum (Al), is considered as a potential alternative to Al in the automotive industry to reduce component weight significantly. Magnesium also has a high strength-to-weight ratio and a high impact resistance. However, some of the major drawbacks of Mg alloys limiting their use in the industry are their inadequate mechanical properties and poor workability relative to Al alloys.[1]

Improving the mechanical properties of Mg alloys will augment their use for more demanding industrial applications. Grain refinement can significantly improve mechanical properties and workability of Mg alloys through achieving fine and uniform grain structure, improving morphology and uniform distribution of secondary phases.[2]

Grain Refinement of Mg and Its Alloys

Depending upon whether they are alloyed with Al, Mg alloys can be generally classified in two groups: i) Al-free such as ZE41 and ZK60 and ii) Al-bearing such as AM50, AM60 and AZ91.[3] The AZ91 series of alloys are the most popular and preferred Mg alloys in the industry, because they have the best combination of castability, mechanical strength and ductility.[4] Grain refinement of Mg alloys can be achieved through a number of physical means, which can be classified under three major techniques: i) thermal ii) mechanical and iii) chemical. Thermal techniques involve rapid cooling and superheating. Agitation of the melt during solidification is a typical example of a mechanical technique. The addition of alloying elements and nucleating agents characterizes chemical grain refinement.[1-3, 5-10] Due to its process simplicity and efficiency, the chemical grain refinement techniques have become the most popular methods of grain refinement of Mg alloys in the casting industry.

Zirconium (Zr) containing refiners are exceptionally effective for Al-free Mg alloys, and corresponding techniques are common practice in the casting industry. Unfortunately, the grain refining efficiency of Zr is poor with Al-bearing Mg alloys, as Al and Zr form stable intermetallic phases which are ineffective as nucleants for Mg grains.[3] One proven solution to this efficiency problem of Al-bearing Mg alloys is the addition of different carbon-containing agents, which have a lower operating temperature and lower tendency to fading[11] than many nucleating agents. Carbon can be effectively introduced to Mg-Al alloys in various forms, such as hexachloroethane (C_2Cl_6), hexachlorobenzene (C_6Cl_6), paraffin wax, lamp black, carbonaceous gases, etc.[12] Different carbides like CaC_2,[12] Al_4C_3,[13,14] SiC[15,16] and carbonates like $MgCO_3$[17,18] have also been successfully used. Previous studies suggest that CaC_2 and C_2Cl_6 were the most effective in the grain refinement of MgAl alloys. However, these refiners may cause environmental problems[3] due to the release of greenhouse gases. This environmental concern warrants the development of alternative grain refiners for Mg-Al alloys.

Over the past few years, a significant number of publications related to grain refinement of Mg-Al alloys have been produced. Some of the potential and effective Mg-Al grain refiners that have resulted from the research are: strontium (Sr),[19,20] boron (B),[21] Al-Ti-B,[22] AlN,[23] calcium (Ca),[5, 24, 25] manganese (Mn),[25,26] rare-earth elements like cerium (Ce)[27] and yttrium (Y).[28] However, in spite of success with previous refiners, there is still no universally accepted refiner for Mg-Al alloys that is environmentally friendly, reliable and easy to apply.[3,21] As such, there is a need to develop effective and environmentally friendly grain refiners for Mg-Al alloys.

Fu et al.[10] examined ZnO as a potential grain refiner for pure Mg and Mg-3 wt.% Al. Using the edge-to-edge matching model ZnO was found to have similar crystallographic parameters to pure magnesium. The edge-to-edge matching model is a computer based program used to examine actual atom matching of two compounds of known crystallography, across an interface between any two phases.[29] In spite of some weakening effect due to instability of this oxide, significant grain size reductions from 1100 µm to 410 µm for pure Mg were observed after an addition of 3 wt.% ZnO. Assuming that the added 3 wt.% ZnO completely reduced, this would be akin to adding 2.5 wt.% Zn solute to the melt. The average grain size of Mg-2.5 wt.% Zn was 510 µm which was larger than that of the pure Mg with 3 wt.% ZnO addition. This postulated that ZnO particles make a contribution to the grain refinement of pure Mg.[10] Lee[30] carried out a preliminary study of ZnO in AZ91E alloy and found some encouraging results. There is a need to carry out a detailed study of the effect of ZnO addition on grain refinement in AZ91E and Mg-9 wt.% Al alloys.

Present Study

In this research, an extensive study of the effect of ZnO in Mg alloys bearing 9 wt.% Al (AZ91E commercial alloys and Mg9 wt.% Al binary alloy) was carried out to examine the effectiveness of ZnO as a potential grain refiner and to determine its refining mechanism.

Experimental Procedure

Materials

In this experiment, commercial AZ91E Mg alloy and binary Mg-9 wt.% Al alloy were used. The AZ91E alloy was received as ingots and the actual analysis from the supplier is given in Table 1.

Table 1. Composition of AZ91E Alloy (wt.%)

Elements	wt.%
Al	9.3
Zn	0.65
Mn	0.24
Ce	0.01
Cu	0.005
Fe	0.002
Ni	0.0009
Mg	Balance

The Mg-9 wt.% Al alloy was prepared using commercial purity Mg (99.8 wt.%) and Al (99.7 wt.%). The ZnO grain refiner was received as powder with a purity of 99% (particle size : < 1 µm).

Casting Procedure

The ZnO, molds and all the accessories used in this casting process were preheated (Table 2). The AZ91E and Mg-9 wt.% Al were melted at 750°C (1382°F) in a steel crucible (diameter: 100 mm/ 3.94 inch and height: 50mm/ 5.91 inch) using an electrical resistance furnace with CO_2 cover gas at the flow rate of 15 SCFH to protect from melt oxidation. Varying levels (0, 0.25, 0.5, 0.75, 1, 2, 3 wt.%) of ZnO were added to the melt at 750°C (1382°F) and stirred with a carbon coated steel propeller coupled with a hand drill machine for 30 sec. After stirring, the melt was held in the furnace for holding times of 5 or 60 minutes. Oxide layers that formed on the top of the melt were skimmed before pouring at a temperature of 720ºC (1328°F). The molten Mg alloys were then poured into the graphite molds (diameter: 40 mm/ 1.57 inch and height: 50 mm/ 1.97 inch), which were preheated to 750°C (1382°F) to reduce the effect of cooling rate on grain refinement. Immediately after pouring, the moulds were covered with a steel plate to avoid oxidation and the temperature data was collected with embedded thermocouples. The castings were also protected with CO_2 during solidification. A schematic of the casting setup is shown in Fig. 1. Cast samples were allowed to cool in still air. The graphite mold casting parameters are summarized in Table 2.

A K-type thermocouple was inserted into the mold (12 mm below steel cover plate) to collect thermal data during the solidification process through a data acquisition system at a sampling rate of five data points per second. For repeatability, three graphite mold castings were prepared for each pour and one repeat pour was conducted for a total of six graphite mold castings for each condition shown in Table 2.

Table 2. Graphite Mold Casting Parameters

Parameter	Values
Addition level (wt.%)	0, 0.25, 0.5, 0.75, 1, 2, 3
Addition temp. (C/F)	750/1382
Holding time (min)	5,60
Preheat temp.(C/F)	Graphite mold-750/1382
	Grain refiners-250/482
Pouring temp.(C/F)	720/1328

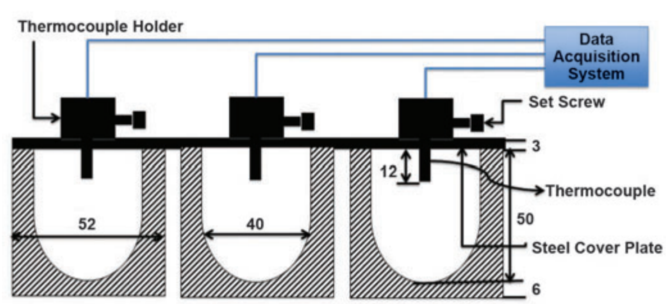

Figure 1. Casting set-up in graphite mold (dimensions in mm).

Optical and Scanning Electron Microscopy

The cast samples were then sectioned for optical (OM) and scanning electron microscopy (SEM). A schematic showing the test surface is as shown in Fig. 2.

Sectioned cast samples were then subjected to solution heat treatment at 420°C (788°F) for 24 hours and air quenched to dissolve the $Mg_{17}Al_{12}$ eutectic phase located at the grain boundary and better facilitate grain size measurements. Solutionized samples were first ground with successively finer SiC grinding papers, then polished using Al_2O_3 solution (5 µm), diamond solutions (3 µm and 1 µm) respectively. Polished samples were then etched with a solution of 10 mL distilled water, 10 mL acetic acid, 100 mL ethanol and 6 g of picric acid. The samples were slightly agitated in the etching solution for 30 seconds and then quickly rinsed with ethyl alcohol and dried with compressed air. Microscopy of the samples was carried out using an optical microscope (OM) and JEOL scanning electron microscope (SEM) operating at 20 KV; with energy dispersive X-ray spectroscopy (EDX) attachment. The SEM samples were examined unetched. The linear intercept method was used to measure the grain sizes of the etched samples. A minimum of one hundred grain size readings were taken for grain size measurement of each sample.

Results and Discussion

Grain Refinement of AZ91E Alloy

Figure 3 shows the optical micrographs of as-cast and solutionized AZ91E alloy samples. The as-cast AZ91E, shown in Fig. 3(a) consists of two distinct phases of α-Mg and β-$Mg_{17}Al_{12}$. The grain structure is highly dendritic in nature. After solution heat treatment, the β-$Mg_{17}Al_{12}$ is dissolved and the grain boundaries are clearly visible as shown in Fig. 3(b).

Figure 4 shows the etched surface of the base AZ91E alloy and AZ91E + 0.75 wt.% ZnO addition which revealed significant reduction of grain size with ZnO addition. The average grain sizes, measured using optical microscope, at different levels of ZnO addition are summarized in Fig. 5. It was found that the base AZ91E had an average grain size of 217 µm. With increasing ZnO addition, the grain size gradually decreased, up to an addition level of 0.75 wt% ZnO. The

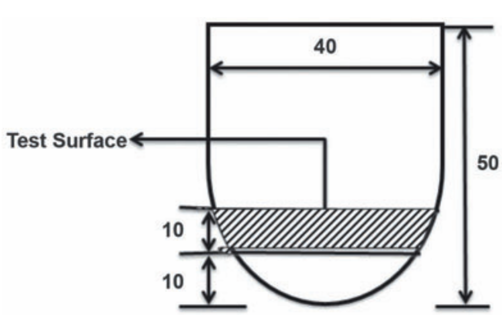

Figure 2. Schematic showing the test surfaces of cast samples (dimensions in mm).

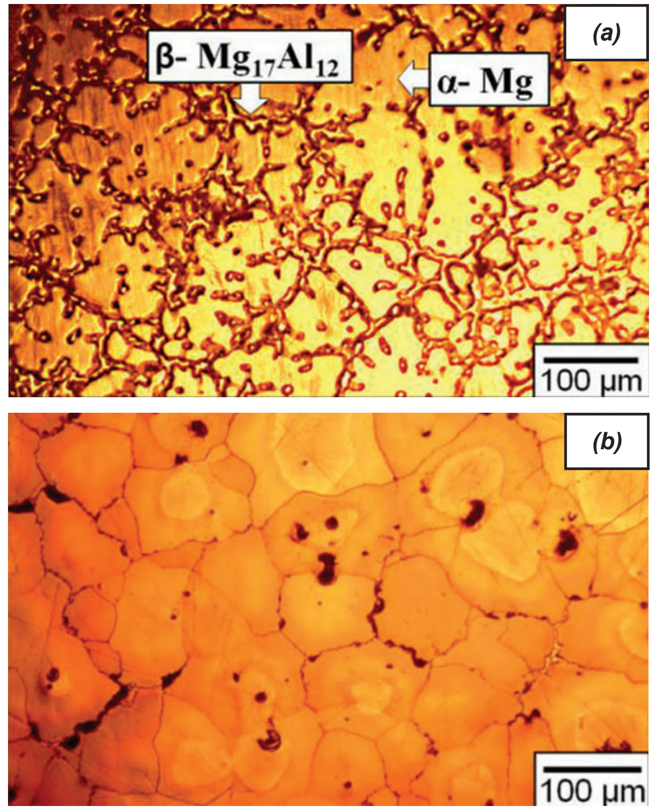

Figure 3. Optical micrograph of AZ91E alloy (a) as cast (b) after solutionized for 24 hours at 420°C (788°F) (average grain size 217 µm).

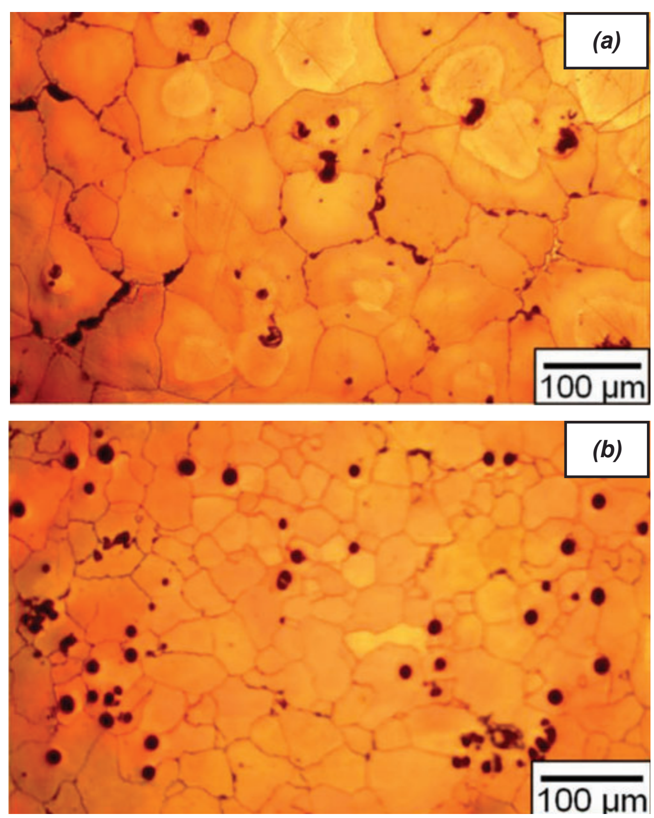

Figure 4. Optical micrograph of (a) base AZ91E alloy (average grain size was 217 µm) (b) AZ91E+0.75 wt.% ZnO (average grain size 108 µm).

average grain sizes at 0.5 wt.% and 0.75 wt.% ZnO were 126 μm and 108 μm respectively. Beyond 0.5 wt.% addition of ZnO (up to 3 wt.%) no significant change in grain size was observed. The slight increase in grain size beyond 1 wt.% ZnO is not significant if we consider the error bars.

Fading in AZ91E Alloy

During grain refinement, holding the melt for a long time after the addition of the grain refiner before pouring, usually leads to develop coarse grain structure, instead of otherwise fine grain structure. This loss of refinement is termed as fading which is usually attributed to either dissolution or settling (or both) of nucleating particles during long holding.[31] A strong resistance to loss of grain refiner efficiency with holding of the melt at elevated temperature for extended periods of time is an important characteristic of a good grain refiner.[32] The fading behavior of ZnO in AZ91E alloy was examined by comparing 5 and 60 minutes after adding 0.5 wt.% ZnO and again 5 and 60 minutes after adding 3 wt.% ZnO. The results are shown in Fig. 6. No significant fading was observed which is consistent with the observations by Fu et al.[10] using pure Mg with ZnO. The grain size remained constant at approximately 125 μm.

Mechanism of Grain Refinement in AZ91E Alloy

An SEM analysis of AZ91E enabled an understanding of refinement mechanism of ZnO. It has been identified by other researchers[29,33] that a good lattice match between nucleating solid and grain refiner will promote heterogeneous nucleation. Both Mg and ZnO have hexagonal closed packed crystal structure. The lattice parameters of Mg are a = 3.2029 Å, c = 5.2000 Å, c/a = 1.6235 and for ZnO are a = 3.2495 Å, c = 5.2069 Å and c/a = 1.602.[34] Using edge-to-edge matching value, the interplaner spacing (dvalue) mismatch between matching planes and interatomic spacing misfit along matching directions are found to be 1.7 and 0.59% respectively[10] for ZnO and Mg. With these crystallographic similarities it was expected that ZnO particles would act as heterogeneous nuclei for α-Mg.

An SEM image of AZ91E alloy with 3 wt.% ZnO is shown at low and high magnifications in Fig. 7(a) and 7(b) respectively. The EDX in Fig. 7(c) clearly indicated the Zn and O peaks. Thus it can be assumed to be ZnO that provided as heterogeneous nucleation site for α-Mg.

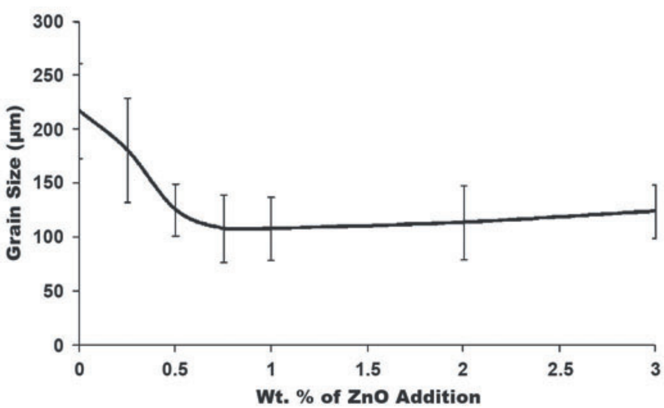

Figure 5. Average grain size of AZ91E alloy with various ZnO addition levels.

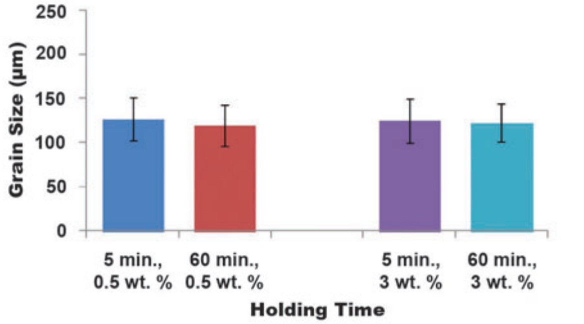

Figure 6. Fading effect of ZnO in AZ91E at different holding times and addition levels.

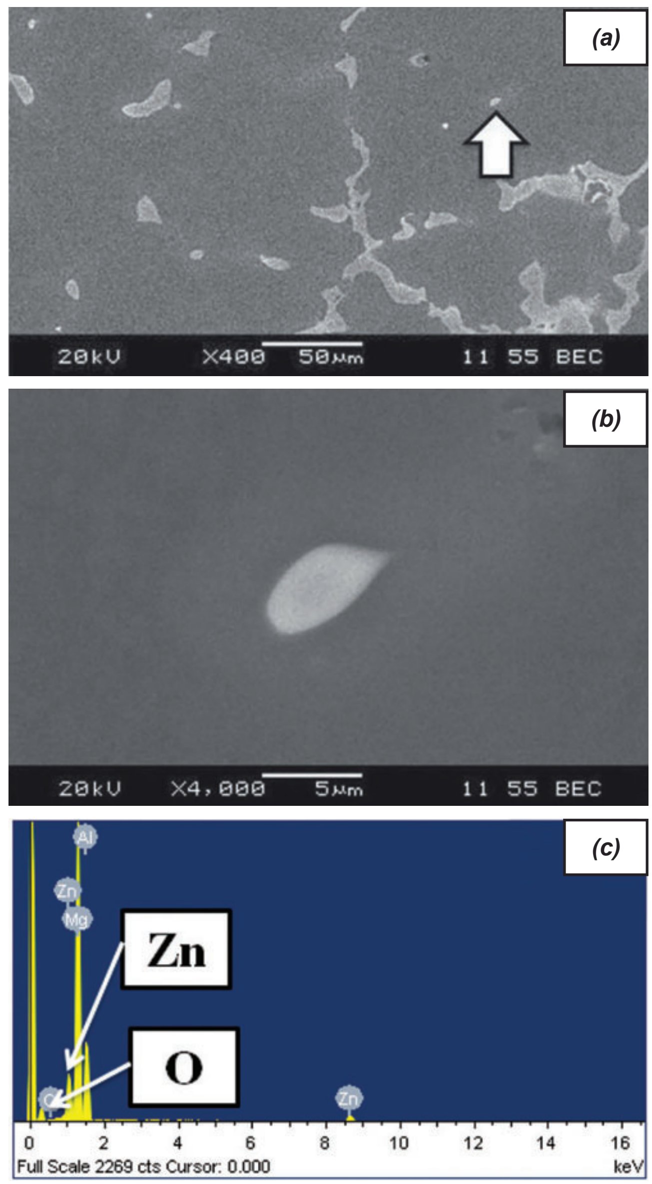

Figure 7. SEM image of AZ91E with 3 wt.% of ZnO (a) at low magnification and (b) at high magnification and (c) corresponding EDX image of particle shown in (b).

Thermal Analysis of AZ91E Alloy

The cooling curves for the base AZ91E alloy and AZ91E with 0.5 wt.% ZnO are shown in Fig. 8. By analyzing the cooling curves, it was found that the base AZ91E alloy had an apparent undercooling of 0.4°C / 0.7°F for primary phase nucleation. The undercooling was measured as the dip in temperature of the cooling curve just after solidification beginning temperature (~595°C / 1103°F). With the addition of ZnO, no undercooling was observed from the generated cooling curves further indicating that the refinement mechanism was primarily heterogeneous nucleation by ZnO.

The freezing range (FR) of the alloys with different levels of ZnO is presented in Table 3. The FR was measured as the difference between the liquidus and solidus temperatures determined from the cooling curves. For base AZ91E alloy, FR was 166.8°C (300.2°F), whereas after 3 wt.% addition of ZnO FR was 169.5°C (305.1°F). These increased FR with ZnO addition is an indication that the ZnO is changing the solidification behavior of the alloy.

Along with an increase in FR with the increase of ZnO addition, the solidus temperature decreased as shown in Fig. 9. A similar trend was also observed by Wang et al.[35] while adding different addition levels of Zn in Mg-Al alloys. As such, the trends may be attributed to increased solute level in the alloy with increasing addition of ZnO to the alloy.

Table 3. Freezing Range of AZ91E Alloy at Different Addition Levels of ZnO

wt.% of ZnO	FR (˚C/˚F)	Std. Dev.(+/-)
0	166.8/300.2	2.14
0.25	166.6/299.9	1.29
0.5	166.8/300.2	0.23
0.75	168.6/303.5	0.91
1	168.5/303.3	1.41
2	171.0/307.8	0.83
3	169.5/305.1	1.27

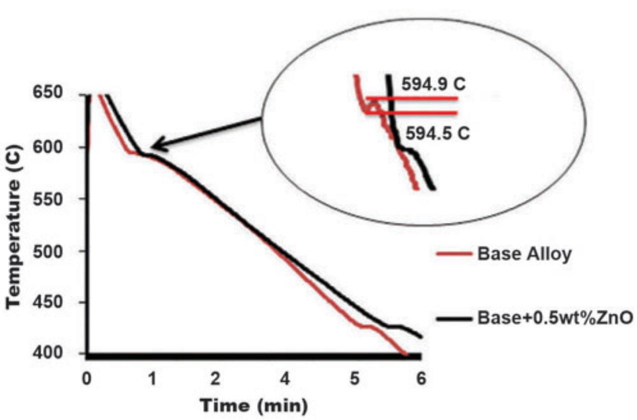

Figure 8. Cooling curve of base AZ91E alloy and AZ91E with 0.5 wt.% ZnO. Enlarged region as indicated is shown in the inset.

This trend of increased Zn solute with addition of ZnO to AZ91E prompted investigation of the effect of ZnO on binary Mg9 wt.% Al. Since AZ91E already contains about 0.65 wt.% Zn, the effect of solute Zn that came from ZnO in AZ91E during solidification process will be difficult to differentiate. By using Mg9 wt.% Al the effect of solute Zn from ZnO can be very easily determined which will give an account of the effect of ZnO in AZ91E alloy.

Grain Refinement In Mg-9 Wt.% Al Alloy

Figure 10(a-b) shows the optical microscopy of a solution treated base Mg-9 wt.% Al alloy and with 1 wt.% addition of ZnO. All the casting parameters were kept the same as the conditions used for the AZ91E castings. Optical microscopy of the Mg-9 wt.% Al alloys revealed that the average grain size of the base Mg-9 wt.% Al binary alloy was 288 μm which was approximately 24% larger than that of AZ91E alloy. This

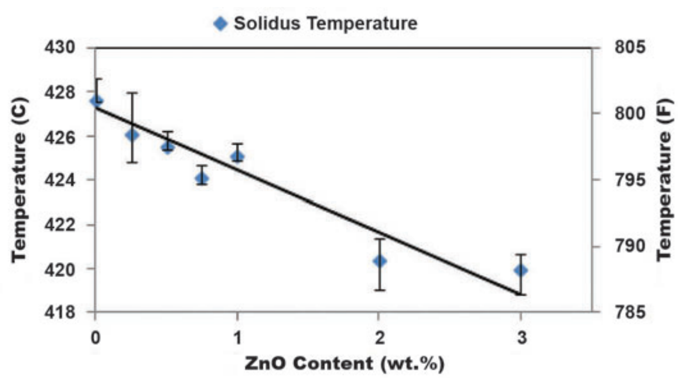

Figure 9. Solidus temperature of AZ91E with ZnO content.

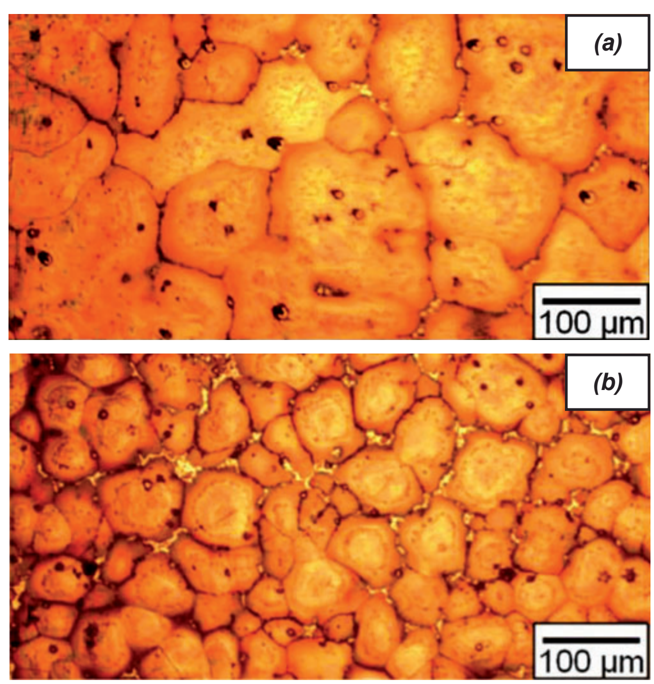

Figure 10. Microstructure of Mg-9 wt.% Al binary alloy after solution heat treatment (a) base alloy (average grain size-288 μm) (b) with 1 wt.% ZnO addition (average grain size-121 μm).

was likely due to the combined effect of Zn and Mn in the AZ91E alloy. Previous research has shown that that both Zn[10] and Mn[26] have a grain refining effect on Mg-Al alloys.

Mg-9 wt.% Al binary alloy castings with 0.5, 1, 2 and 3 wt.% of ZnO were produced. Figure 11 shows the average grain size of Mg-9 wt.% Al with different addition levels of ZnO. A similar grain refinement trend to that of AZ91E (Fig. 5) was observed for Mg9 wt.% Al alloy. Maximum grain size reduction was found at 3 wt.% addition of ZnO (93 µm), although beyond 0.5 wt.% addition of ZnO (121 µm) the grain size reduction was not very significant.

For complete reduction of ZnO to Zn, the Zn concentration with 0.5 wt.% addition of ZnO to AZ91E (initially containing 0.65 wt.% Zn) would be higher than the same addition to binary Mg-9 wt.% Al (akin to 0.4 wt.% Zn). In this experiment, the mean average grain sizes with 0.5 wt.% ZnO addition to AZ91E and Mg-9 wt.% Al were similar at 126 µm and 121 µm respectively. This suggests that the grain refinement achieved by the ZnO particle addition is greater than that gained by an equivalent addition of Zn solute.[36]

Fading in Mg-9 Wt.% Al Alloy

The fading behavior of ZnO in Mg-9 wt.% Al alloy was examined by comparing 5 and 60 minutes after adding 0.5 wt.% ZnO and same 5 and 60 minutes after adding 3 wt.% ZnO. The results are shown in Fig. 12. The average grain sizes at 0.5 wt.% ZnO addition after 5 minutes and 60 minutes were 121 µm and 126 µm respectively. With 3 wt.% ZnO addition average grain sizes after 5 minutes and 60 minutes were 93 µm and 103 µm respectively. No significant fading was observed which is consistent with the results of AZ91E alloy (Fig. 6).

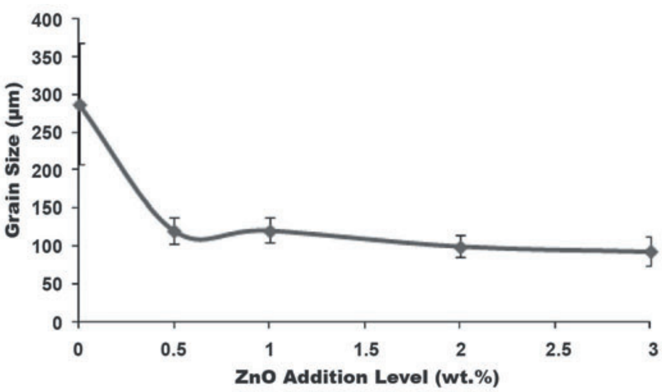

Figure 11. Average grain size of Mg-9 wt.% Al binary alloy with various levels of ZnO addition.

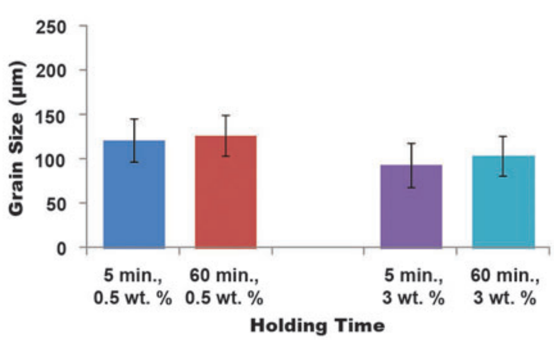

Figure 12. Fading effect of ZnO in Mg-9 wt.% Al binary alloy at different holding times and addition levels.

Mechanism of Grain Refinement in Mg-9 Wt.% Al Alloy

The SEM and corresponding EDX results of base Mg-9 wt.% Al are shown in Fig. 13. The sample consisted of α-Mg matrix (Point A in Fig. 13) and β- $Mg_{17}Al_{12}$ (Point B in Fig. 13).

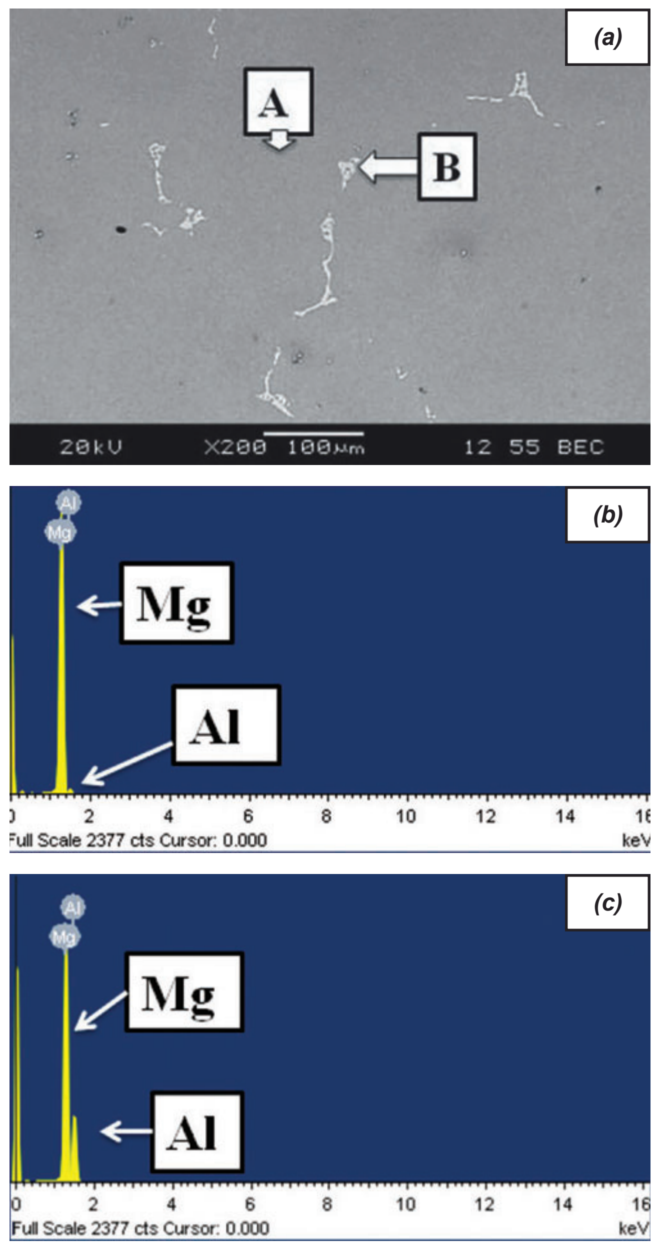

Figure 13. (a) SEM image of base Mg-9 wt.% Al showing α-phase and β-phases (b-c) shows the EDX analysis of point-A and point-B respectively.

With the increased ZnO addition, the β-phase was found to be increasingly enriched with Zn solute as shown in Fig. 14. This Zn solute is thought to have been liberated from ZnO because it reacted with the Mg according to Eqn. 1.[10]

$$ZnO + Mg \rightarrow MgO + Zn \qquad \text{Eqn. 1}$$

Therefore, since only a small amount of added ZnO particles act as nucleating sites, it is possible that some ZnO may have dissociated, which in turn, introduced Zn into the melt.

Figure 14 shows an SEM image and corresponding Zn element maps of base Mg-9 wt.% Al and with 1 wt.% , 2 wt.% and 3 wt.% of ZnO addition, respectively. It is evident from the image that with an increased ZnO content in Mg9 wt.% Al, increased Zn solute is observed (in Fig. 14-b some background noise can be seen though Zn is absent). This supports

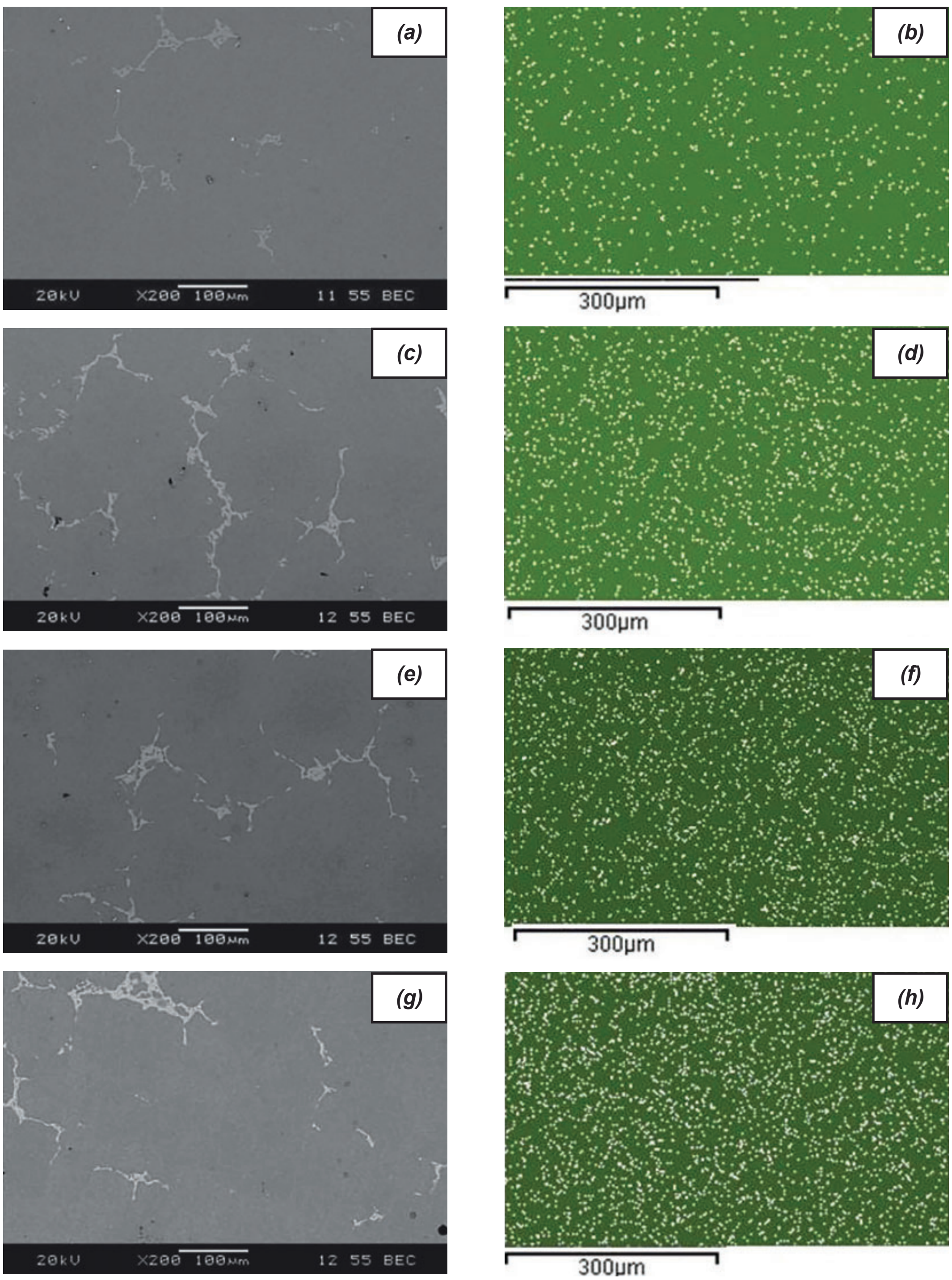

Figure 14. SEM image and corresponding Zn element map of (x200) of Mg-9 wt.% Al with (a-b) no addition of ZnO, (c-d) 1 wt.% ZnO addition, (e-f) 2 wt.% ZnO addition (g-h) 3 wt.% ZnO addition.

results from thermal analysis suggesting increased FR and decreased solidus temperature with ZnO addition. Increased divorcing of intermetallic phases with additions of ZnO is also clearly visible, which is indicative of increased Zn solute presence and effective grain refining capability of ZnO.[11]

Figure 15 shows the SEM and EDX results of Mg-9 wt.% Al with 2 wt.% addition of ZnO. The bright white spots seen embedded within the $Mg_{17}Al_{12}$ indicate enriched Zn. Zn has a relatively very high growth restriction factor of 5.31 in Mg.[3] This high growth restriction factor likely restricted the α-Mg grain growth by generating constitutional undercooling in solidliquid interface, thus limiting the size of the grain.[5]

Thermal Analysis of Mg9 Wt.% Al Alloy

Thermal analysis of Mg-9 wt.% Al alloy with ZnO addition revealed the same characteristics to that of AZ91E alloy. By analyzing the generated cooling curves, no undercooling was observed with the addition of ZnO for all addition levels. The freezing range (FR) of the alloys with different levels of ZnO measured from the cooling curves is presented in Table 4. For base Mg-9 wt.% Al alloy, FR was 160.0°C (288°F), whereas after 3 wt% addition of ZnO FR was 171.3°C (308.4°F). An increased FR with ZnO addition indicates the similar change in solidification behavior to that of AZ91E alloy.

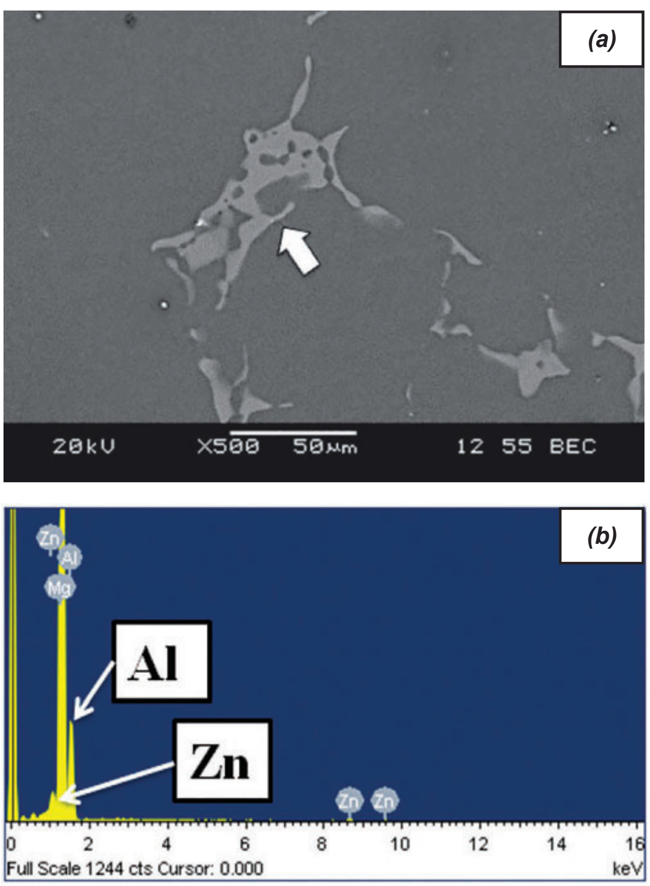

Figure 15. Mg-9 wt.% Al with 2 wt.% ZnO (a) SEM image and (b) EDX results at location indicated by arrow.

Along with an increase in FR with the increase of ZnO addition, the solidus temperature decreased as shown in Fig. 16. This decreased trend of solidus temperature is also similar to AZ91E alloy (Fig. 10). Similar thermal behaviors for AZ91E and Mg-9 wt.% Al alloys of ZnO reinforces that the grain refining mechanism of ZnO for both the alloys appears to be via two routes: 1) ZnO act as a nucleating site and 2) ZnO reacts with Mg according to Eqn. 1 increasing Zn solute in the melt providing growth restriction.

One possible drawback to using ZnO as grain refiner is that it may promote the formation of MgO. Even with skimming prior to casting, some of MgO may remain in the melt affecting the mechanical properties of the casting.

Conclusions

This study showed that ZnO is a reliable and effective grain refiner for AZ91E and Mg-9 wt% Al binary alloys. It is expected that this efficient and environmentally friendly grain refiner would stimulate the use of these alloys. The grain refinement effects of ZnO are summarized as follows:

1. For AZ91E alloys, maximum grain size reduction was found at 0.75 wt.% addition of ZnO (108 µm) and for Mg-9 wt.% Al binary alloy maximum reduction was found at 3 wt.% addition of ZnO (93 µm).
2. No fading effect was observed for up to 60 minutes of holding time and for 3 wt.% addition level of ZnO to both AZ and binary alloys.

Table 4. Freezing Range of Mg-9 wt.% Al Alloy at Different Addition Levels of ZnO

wt.% of ZnO	FR (˚C/˚F)	Std. Dev.(+/-)
0	160.0/288.0	2.9
0.5	166.1/299.0	1.9
1	167.2/300.9	1.78
2	169.4/304.9	1.45
3	171.3/308.4	1.27

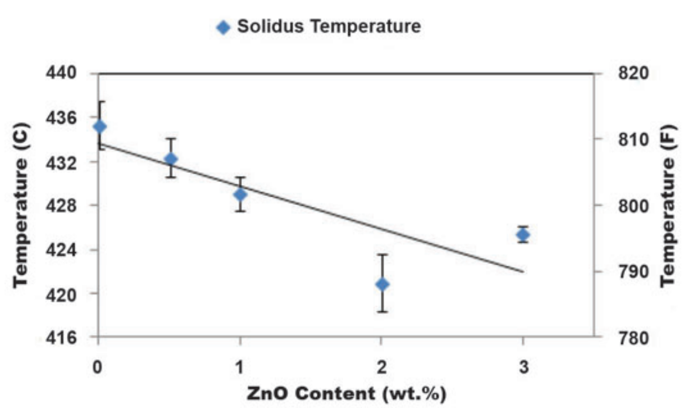

Figure 16. Solidus temperature of Mg-9 wt.% Al with ZnO content.

3. Grain refinement was attributed heterogeneous nucleation due to ZnO and grain growth restriction of Zn (which was liberated during ZnO dissociation) on α-Mg matrix.

Acknowledgments

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Technical Review & Discussion

Grain Refinement of AZ91E and Mg-9 Wt.% Al Binary Alloys Using Zinc Oxide

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Reviewer: In Figure 14, the Zn element map shows Zn content in photograph B even when none has been added according to the caption. What are we seeing here?

Authors: *The white spots we can see in Fig. 14-b (the Zn element map where no Zn was present) are due to background noise. We have reconfirmed this carrying out EDX mapping for elements like tungsten, copper, chromium and titanium on the same sample. The results were similar.*

Reviewer: Much of this paper covers similar ground as the Fu paper (Reference #10). Interestingly, Fu et al. comes to a different conclusion that "the reduction reaction of ZnO to Zn by Mg limits the efficiency of ZnO as a grain refiner". In the Fu experiment, they got about 80% of the grain refining effect by just adding Zn which is a whole lot easier than mixing powder into a melt.

Authors: *Thank you for your comment. The reviewer brings to light an important point regarding the practical usage of ZnO for Mg grain refinement. Fu et. al.*[10] *found that the pure Mg casting had an average grain size of 1100* µm which decreased to 410 µm with *3 wt.% ZnO addition. Additional material and additional Reference #36 in the revised manuscript should provide a better explanation. The authors acknowledge that the reduction of ZnO in Mg alloys limits its efficiency. Possible avenues for future research could involve optimization (addition temperature, holding time, addition method) to reduce the reduction of ZnO and maximize the potential as a nucleating particle.*