Novel Approaches to Grain Refinement of Magnesium Alloys

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B. Eng., M. Eng.
Abstract

Grain refinement of cast metals through inoculation has been one of the most favourable approaches in the industry due to its convenience, low cost and reproducible good results in obtaining fine equiaxed as-cast microstructures. Grain refinement is also considered one of the most effective approaches to simultaneously improve castability, strength, ductility and formability of metals. Since the 1990’s, Mg has been one of the most important structural materials, particularly in the automotive industry, due to its abundance in the earth’s crust, lightness and good castability. However, as-cast Mg is usually associated with low strength, ductility and creep resistance. In the last couple of decades, grain refinement of Mg alloys has been an active research topic, because achieving finer grains is found to be increasing both strength and ductility of the alloys. So far, it is believed that grain refinement by inoculation can be achieved through restricting the grains growth by controlling the constitutional undercooling during solidification or through increasing the nucleation rate in the melt or both. However, a number of important details in the grain refinement mechanism are still unknown and there has not been a unique model found in the literature that can fully satisfy all experimental findings. In addition, most of the developed grain refiners are not as effective as zirconium which is considered the most effective grain refiner for Mg so far; but it does not work with Mg-Al alloys which form the majority of commercially used Mg alloys.

In order to design a new grain refiner, growth restriction factors (Q-values) of a number of solutes that have not been found in the literature were calculated in binary Mg alloys. Following that, calculations using the edge-to-edge crystallographic matching (E2EM) model predicted FCC-CaO as an effective nucleant for the HCP-Mg. Casting experiments were then undertaken through addition of various amounts of CaO into the Mg melts. As-cast optical micrographs showed dramatic reduction in grains size with CaO particles addition. At 0.3 wt.% CaO addition level, columnar to equiaxed (CTE) transition of Mg alloys was firstly observed. Further CaO addition led to further grain refinement. Through SEM analysis CaO particles were spotted at the centres of the grains, which indicated that CaO particles can successfully nucleate Mg grains. In addition, Ca solute was introduced into the melt through decomposition of some CaO particles, which further improved the grain refinement efficiency. Addition of CaO into Mg-Ca and Mg-Zn alloys led to even more grain refinement; but grain coarsening was obtained in Mg-Al-CaO alloys. The effect of CaO on the mechanical properties of Mg alloys was then studied through preparing two groups of samples (Mg-Ca and Mg-CaO based alloys). Tensile and hardness results showed that both sample groups were strengthened. However, the grain refinement strengthening component was higher in Mg-CaO base alloys.
Fast cooling is another common approach to produce fine as-cast grains. But, a comprehensive study of the effect of cooling rate on the grain refinement of Mg alloys is lacking. To investigate the effect of cooling rate on the microstructure of as-cast Mg alloys, a V-shaped copper mould was designed that produces different cooling rates along its height. Pure Mg, Mg-Al, Mg-Zn, Mg-Zr and Mg-CaO base alloys were then cast using this mould and the as-cast microstructure of the alloys was then investigated. Unlike what was normally expected, results showed that higher cooling rate does not always lead to grain refinement. Mg-1.0wt.%Zr, Mg-1.4wt.%CaO and Mg-3.0wt.%Al alloys suffered from grain coarsening at the tip of the mould, where the highest cooling rate was achieved. It was considered that at high cooling rate, due to the high thermal gradient, the constitutional undercooled zone formed ahead of the solid/liquid interface is smaller. As a result, most of this zone might lie within the nucleation free zone proposed by the interdependence theory. Thus, in this situation grain growth might be favourable over nucleation of new grains resulting in grain coarsening.

Due to the high commercial importance of Mg-Al based alloys, the effects of various tertiary elements addition into Mg-Al based alloys were studied in terms of microstructure and strengthening mechanisms. Silicon, copper, titanium, manganese, calcium and tin solutes were added separately into Mg-3.0wt.%Al and Mg-9.0wt.%Al based alloys in various concentrations. Grain size and hardness were measured for the as-cast alloys. Results showed that the grain refining significance of Sn, Ti or Mn containing alloys is very low. Thus, further solution treatment and aging experiments were designed and performed on Cu, Ca and Si containing alloys. Hardness and microstructure results of the as-solution treated and aged alloys suggested that in Mg-3.0wt.%Al based alloy, only the Ca solute showed a precipitation hardening effect. On the other hand, in Mg-9.0wt.%Al based alloys, Mg_{17}Al_{12} intermetallic compounds still played a major role in precipitation hardening.

In summary, the investigations presented in this PhD thesis have contributed to understanding the mechanism of grain refinement in Mg alloys. Based on the results, it is concluded that in order to design a successful grain refiner for Mg alloys many parameters need to be considered. In addition, the current work highlights the major role played by cooling rate in controlling the grains size. Finally, it comprehensively discusses the effects of various tertiary solutes on Mg-Al based alloys.
Declaration by author

This thesis is composed of my original work, and contains no material previously published or written by another person except where due reference has been made in the text. I have clearly stated the contribution by others to jointly-authored works that I have included in my thesis.

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Contributions by others to the thesis

No contributions by others.

Statement of parts of the thesis submitted to qualify for the award of another degree

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At the start of this PhD I would not have imagined that this moment will come to write the final words in my thesis. For the past three and half years, I have lived an amazing journey which resembles one of the major milestones in my life. The journey had its pros and cons, I lived in one the most beautiful places in the world but away from everything and everyone I grew up with; I experienced working in a multinational environment with very highly qualified people and in one of the most professional and prestigious institutes in the world, but I was paid in students rate and living on a right budget. It has been a very interesting journey full of not only hard work, sweat, tears and blood but also laughs, joy, love and happiness. I have spent many nights working and thinking, and others crying, praying, laughing or even fishing. This PhD has changed me and my life for good and I am very happy with the experience and grateful I had it. However, I could have never achieved anything without the people around me who helped me in so many ways to pursue and fulfil this dream. Hence, in the following sentences, I would like to take this opportunity to express my gratitude to them.

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Grain refinement, Magnesium alloys, light metals, casting, grain coarsening, alloying, CaO, cooling rate, V-shaped mould, mechanical properties, edge-to-edge matching model.

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Chapter 1 Introduction

1.1. Magnesium, magnesium alloys and their applications

Magnesium (Mg) is well-known for its low density (1.74 gm/cm$^3$) and considered as the lightest structural metal on earth. Also it is the 6th most abundant element representing 2.7% of the earth’s crust [1]. During World War II a rapid increase in Mg production was sparked mainly for aviation and weaponry production [2]. After the war, Mg was unable to compete with other metals, aluminium (Al) in particular, economically in terms of production cost and technologically in terms of mechanical properties. Hence, its production was affected by a drastic hit and decreased due to the closure of most of the main manufacturers. Since the 1990’s, the automotive and aerospace industries showed high interest in Mg and its alloys aiming to reducing fuel consumption through weight reduction. Thus, the potential of Mg and its alloys was seen again and Mg was recognised as a structural material [2]. Since then, Mg productions have been increasing each year. In the last 10 years, Mg global production has spiked from 690,000 tons in 2006 to 1,010,000 tons in 2016 [3, 4].

Pure Mg is very soft and has almost no engineering applications. Hence, in the last couple of decades considerable research efforts have been subjected into developing Mg alloys in order to overcome these limitations. For instance, it has been found that surface treatment is an effective approach in improving corrosion and creep resistance [5, 6]. In addition, materials scientists and engineers have tried many strengthening mechanisms to increase the mechanical properties of Mg alloys. Some of which could be achieved through melt treatment or post casting treatment to metal ingots such as cold working. Among these mechanisms, grain refinement strengthening has been a very effective approach as it simultaneously improves strength, ductility and formability of Mg alloys. Grain refinement can be achieved through thermal-mechanical treatment of the as-cast ingots or melt treatment during the casting process. While the former requires higher energy and more costive; melt treatment, particularly through inoculation, is always preferred in industry due to its ease of application and low cost.

1.2. Advantages of grain refinement:

Grain refinement improves mechanical properties through two approaches. One, grain refinement converts columnar grains, which are associated with anisotropic properties and texture, into equiaxed, giving better isotropic properties to the metal. Second, fine grains are associated with higher strength and toughness through increasing grain boundaries that work as stoppers to dislocations motions. This is particularly essential for Mg due to its HCP crystal structure. Through
revisiting the well-established Hall-Petch equation [7], the effect of grain refinement hardening can be explained. The equation is expressed as follows:

\[ \sigma_{\text{eff}} = \sigma_0 + k d^{-1/2} \]

Where \( \sigma_0 \) is the intrinsic lattice resistance to basal slip, \( k \) is a strengthening coefficient and \( d \) is the size of the grain. Smaller \( d \) value means more grain boundaries, which in return restrict dislocation motion in the metal and hence strengthen it. As for Mg, experimental work showed that \( \sigma_0 = 11 \) MPa for Mg [8]. But, \( k \) value varies from 0.22-0.37 MPa.m\(^{1/2}\). In the same study, it was assumed that \( k \) value varies linearly between the upper and lower values as solute concentration increases. Moreover, a fine grains structure helps in dispersing brittle intermetallic compounds. As a result formability is also improved.

One of the main task is to improve the creep resistance of Mg alloys. At elevated temperatures (~ 0.5 \( T_m \)), the creep rate under steady state conditions is expressed by the following equation:

\[ \dot{\varepsilon} = \frac{A D G b}{k T} \left( \frac{b}{d} \right)^p \left( \frac{\sigma}{G} \right)^n \]

Where \( A \) is a dimensionless constant, \( D \) is the diffusion constant \( (=D_0 \exp(-Q/RT)) \) where \( D_0 \) is a frequency factor, \( Q \) is the activation energy, \( R \) is the gas constant and \( T \) is the absolute temperature, \( G \) is the shear modulus, \( b \) is the Burgers vector, \( k \) is Boltzmann’s constant, \( p \) is the exponent of inverse grain size, \( \sigma \) is the applied stress, and \( n \) is the exponent of stress [9]. For metals with coarse grains, the flow behaviour at elevated temperatures is intergranular in nature and \( p=0 \) but when the grain size is reduced, other flow processes become effective which are dependent on the grain size such as Nabarro-Herring and Coble diffusion creep and super plasticity [10]. Hence, through achieving finer grains, creep resistance and high temperature mechanical properties of the alloys are improved.

Not only grain refinement can improve mechanical properties and formability, but also castability. During solidification, hot cracking is normally the result of segregation of low melting temperature inclusions along the grain boundaries. This segregation can be diluted through obtaining finer grains. Thus, grain refinement can also reduce hot cracking. Also, the maximum pore length in the as-cast ingots is affected by grain size and it was found that with finer grains structure the maximum pore length is reduced [11, 12]. Also, grain refinement improves feeding during casting through obtaining a fine evenly distributed intermetallic compounds.
1.3. Grain refinement in Mg alloys and the current challenges

The currently available grain refinement techniques for Mg alloys can be divided into two main categories. One is the thermal–mechanical treatment for solid metal, which leads to plastic deformation and dynamic recrystallization, and hence, small equiaxed grains can be achieved. Equal channel angular pressing (ECAP) process is a typical example for plastic deformation grain refinement [13]. The other category is to achieve grain refinement during casting process either by stirring prior to casting or during solidification, such as the magnetic and ultrasonic treatment, or through melt treatment, such as inoculation or cooling rate control. Although very fine grains can be obtained through plastic deformation, the process is rather costive, relatively slow and requires high energy. On the other hand, melt treatment is a cheaper and easier process; thus, it is usually preferred in industry. Also, obtaining as-cast ingots with fine grains reduces the amount of energy needed if further plastic deformation is required. Generally, magnetic and ultrasonic treatments are not practically preferred techniques in industry especially in high production foundries. The reason behind that is the variation in grain size obtained in the ingots depending on the distance from the source; i.e. within the same ingot, finer grains are obtained in the areas closer to the source while coarser grains are obtained away from it. Alternatively, grain refinement through inoculation is more preferred due to its reproducible results, ease in application, low cost and the uniform equiaxed grains obtained through the whole cast ingot.

Grain refinement by inoculation is generally achieved through the addition of solute elements and/or increasing the number density of heterogeneous nucleation sites in the melt through addition of foreign nucleants or the formation of in-situ particles during solidification. The mechanism of solute growth restriction of grains can be summarised as follows. During solidification, segregation of the solute atoms ahead of the solid liquid (S/L) interface leads to the formation of a constitutionally supercooled zone at the front of the interface. This supercooled zone may act as driving force to promote new nucleants to nucleate new grains within the zone, and therefore inhibit the growth of the existing grain. The newly formed grains also restrict the growth of the early formed grains. As a result, the required equiaxed grains structure is obtained.

Grain refinement in Mg alloys has been extensively studied in the last couple of decades. However, a number of issues are still arising in the literature that have not been solved yet. Up to date, zirconium (Zr) is considered as the best grain refiner for Mg. But, Zr inoculation grain refinement process has some major limitations. In addition to its high cost compared to other elements, zirconium particles settle at the bottom of the crucible due to their higher density than that of Mg melt which requires stirring of the melt prior to casting to ensure their even distribution throughout the melt. More importantly, zirconium does not work with
aluminium/silicon/manganese containing Mg alloys as it loses its grain refinement efficiency through reacting with these elements to form intermetallics. This largely limits its commercial applications as most commercially used Mg alloys contain aluminium. So far, a number of refiners have been developed for Mg-Al alloys such as Al$_2$Y [14], SiC [15] and Al$_4$C$_3$ through the carbon inoculation process [16]. However, none of these refiners is as effective as Zr in pure Mg. Also, there is a big gap in the literature into understanding the mechanism of grain refinement. Many models were developed in order to explain the process but none is able to explain grain refinement in all Mg alloys. Among them, the recent interdependence theory [17] which describes the contribution of secondary nucleation within the constitutional supercooling zone. Even though it combines the role of both solutes and nucleating particles in the melt, more experimental data is needed for its full validation.

1.4. Objectives of this PhD project and thesis outline

The main objectives of this PhD were set to solve some of the issues mentioned in subsection 1.3 and can be summarized as follows:

a) Developing an effective new grain refiner for Mg alloys.
b) Studying the effects of the new grain refiner on the mechanical properties of Mg alloys.
c) Investigating the effects of solutes and potent nucleants under different casting conditions on Mg alloys grains in order to help understanding the grain refinement mechanism in Mg alloys.

In order to achieve these goals, the following tasks will be completed:

1- To carry out in depth investigation on the role of growth restriction factor (Q-value) in binary Mg alloys and calculate the Q values for new binary Mg alloys.

2- To design a novel grain refiner for Mg alloys through correlating its crystallographic matching with Mg matrix using the edge-to-edge crystallographic matching model.

3- To study the efficiency of the new designed grain refiner on the as-cast Mg alloys.
   - Characterize the microstructure using polarized optical microscope (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).
   - Characterize the effect of the new developed grain refiner on the mechanical properties of the as-cast alloys through tensile and hardness testing.

4- To make breakthroughs perform and to provide an insightful conclusions on the role of cooling rate on grain refinement by inoculation process and correlate the results to the currently available models for grain refinement.

5- To finally study the grain refinement strengthening effects of various solute elements on Mg-Al alloys.
To thoroughly achieve these aims, the chapters of the current thesis are divided as follows:

**Chapter 1** (a) lists the advantages of grain refinement, (b) gives a brief introduction on grain refinement techniques particularly in Mg alloys, (c) lists the current arising issues in Mg grain refinement and (d) outlines the objectives of the PhD and thesis framework.

**Chapter 2** (a) provides a comprehensive updated review on the effects of the major alloying elements on the grains of Mg alloys, (b) lists and briefly discuss the major theories and models used in understanding the grain refinement mechanism and (c) lists the Q-values of new binary systems that was not published before. The majority of this chapter’s contents were published in a review papers in 2015.

**Chapter 3** describes the general experimental procedures used throughout the PhD to achieve the current results and outcomes. This includes all the raw materials used, casting procedures, heat treatment, characterisation and analysis of the alloys through tensile and hardness testing, optical microscopy, scanning electron microscopy, focused ion beam and transmission electron microscopy.

**Chapters 4-6** present the research work and outcomes carried out through original work done in this PhD which specifically document the background, experimental procedures, results and discussions of each study. The work provides major achievements in Mg grain refinement and the majority of the results were published in 5 peer reviewed papers specified in each chapter.

**Chapter 7** summarizes the overall outcomes, conclusions and contributions of this PhD research. Following that, it suggests some potentially interesting topics arise from the outcomes of this PhD for future research.
Chapter 2 Literature review

2.1. Chapter overview:

In magnesium alloys, grain refinement is essential for improving castability, formability and mechanical properties. It can be achieved through many processes. Among them, inoculation has been a widely accepted technique for its ease of application, low cost and superior results in the as-cast alloys. In this chapter, the current progress in grain refinement of magnesium alloys is reviewed.

First, the major theories and models proposed to understand the grain refinement mechanism are discussed. This includes models based on the effect of heterogeneous nucleation and others based on the effects of solutes. The Q-values of almost all solutes that can be used in Mg alloys were calculated. The Q-values for some solutes have never been reported before. In this chapter, the effects of the major solutes on grain refinement of cast Mg alloys is also summarized and reviewed. The solutes include Ti, Zr, Ca, Si, Na, Cu, Ag, Sn, Co, Mn and rare earth elements. Finally, the effects of carbon inoculation and other inoculants on as-cast microstructure of Mg alloys are reviewed. The major part of this chapter was published as a review paper entitled “Current research progress in grain refinement of cast magnesium alloys: A review article” in Journal of Alloys and Compounds (2015, vol. 619, pp. 639-651) in 2015. This paper is referred as Paper 1 in this thesis.

Since this review paper was published two years ago, an updated literature review on grain refinement of Mg alloys was done in Section 2.3. The review focuses on the discussions of roles of solutes and inoculants in grain refinement of Mg alloys. This includes of the recently discovered grain refiners for Mg alloys. An additional section (section 2.4) reviews the effects of various hardening mechanisms on the mechanical properties of Mg alloys to cooperate the PhD work in chapters 4 and 6.
2.2 *Associated paper:*

**PAPER 1**

*Current research progress in grain refinement of cast magnesium alloys: a review article*

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Current research progress in grain refinement of cast magnesium alloys: a review article

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Abstract:

Grain refinement of cast magnesium alloys, particularly in magnesium-aluminium (Mg-Al) based alloys, has been an active research topic in the past two decades, because it has been considered as one of the most effective approaches to simultaneously increase the strength, ductility and formability. The development of new grain refiners was normally based on the theories/models that were established through comprehensive and considerable studies of grain refinement in cast Al alloys. Generally, grain refinement in cast Al can be achieved through either inoculation treatment, which is a process of adding, or in situ forming, foreign particles to promote heterogeneous nucleation rate, or restricting grain growth by controlling the constitutional supercooling or both. But, the concrete and tangible grain refinement mechanism in cast metals is still not fully understood and there are a number of controversies. Therefore, most of the new developed grain refiners for Mg-Al based alloys are not as efficient as the commercially available ones, such as zirconium in non-Al containing Mg alloys. To facilitate the research in grain refinement of cast magnesium alloys, this review starts with highlighting the theoretical aspects of grain refinement in cast metals, followed by reviewing the latest research progress in grain refinement of magnesium alloys in terms of the solute effect and potent nucleants.

1. Introduction:

The lightness, good castability and wealth deposition in the earth, make magnesium (Mg) an attractive and promising structural engineering alloy. Magnesium production have been increased from 670,000 tons in 2007 to 910,000 tons in 2013 [1, 2], being in the third place after steel and aluminium in the world annual production of metals. This indicates that magnesium alloys are in high demanding, particularly, in automotive industry as this sector is working to improve the fuel efficiency through weight reduction [3]. However, Mg alloy is also associated with a number of
limitations compared to other metals, such as aluminium alloy. These limitations include low creep resistance, lower tensile properties (strength and ductility), poor workability due to its hexagonal structure, and low wear and corrosion resistance. Generally, surface treatment is an effective approach to solve the wear and corrosion issues [4, 5]. Also, rare earth elements addition is considered as an effective approach to increase the creep resistance and strength. Some examples of the commercially used RE in Mg alloys are gadolinium, neodymium and cerium.

Because of the large difference in solid solubility of gadolinium (Gd) in Mg at high temperature (23.5wt% at 548°C) and at low temperature (3.8wt% at 200°C), a number of Mg-Gd based alloys have been developed. Typical examples are the Mg-6Gd-2Zn-0.6Zr alloy [6], Mg-15Gd-5Y-0.5Zr alloy [7] and Mg-10Gd-2Y-0.2Zr alloy. In addition, neodymium (Nd) and cerium (Ce) are also commonly used as alloying elements. These alloys include Mg-Ce-Nd system [8], the modified WE54 alloy, Mg-3Y-2Nd-1Zn-1Mn alloy [9] and Mg-6Zn-1Y-0.6Ce-0.6Zr alloy. Although these alloys have superior mechanical properties and a yield strength of 470 MPa can be achieved [10], high content of RE leads to two issues. One is the increase of cost due to the addition of expensive RE. Thus, this type of alloys is hard to be accepted by ordinary car manufacturers (except for the racing and luxury cars). Another issue is the increase of density of the alloys. For example, adding 15wt% Gd increases the density to 2.66 (the density of Gd is 7.9 g/cm³, and Mg has the density of 1.74 g/cm³). In this case, the advantage of lightness of Mg alloys does not exist anymore. Hence, material scientists and engineers have been seeking an alternative approach to overcome the problems associated with Mg alloys. Grain refinement has been considered as one of the most effective approaches. This is not only because grain refinement can simultaneously improve strength, toughness and ductility, reduce casting defects, such as segregations and porosity, but also because it eliminates the columnar structure, and therefore increases the quality of wrought alloys through improvement of formability [11]. In the past couple of decades, grain refinement of Mg alloys has been one of the most active research topics.

The currently available grain refinement techniques for Mg alloys can be divided into two basic approaches. One is the thermal-mechanical treatment upon solid Mg alloys, which leads to plastic deformation and dynamic recrystallization, and hence, small equiaxed grains can be obtained. Details about plastic deformation method can be found in references [12-14]. The other approach is to achieve grain refinement during casting process either by stirring, such as ultrasonic treatment [15], or through melt treatment, such as inoculation. The early succussed melt treatment for grain refinement of Mg-Al based alloys includes the superheating method [16], the Elfinal process [17] and carbon inoculation [18], etc. So far, there are still some arguments on the grain refining mechanism underlying these processes, and more detailed discussions can be found in previous reviews [11, 19, 20].
Inoculation is considered as a successful melt treatment approach to effectively achieve grain refinement. This refers to adding grain refiners or/and small amount of solute elements to promote heterogeneous nucleation and restrict the grain growth. Up to date, zirconium inoculation remains the highest in grain refining efficiency for cast Mg. More than 80% grain size reduction was achieved after adding 0.15 wt.% zirconium to the melt [21]. Unfortunately, zirconium does not work with aluminium/silicon/manganese containing Mg alloys. The reason behind that is it usually loses its grain refining potency due to the formation of intermetallic phases with Al, Mn and Si. In addition, it is rather costive to prepare master alloy containing zirconium. Particularly, as Mg-Al system has been the basis of the most commonly used cast alloys in industries [22], extensive research work has been done to seek effective, low cost and practical grain refiner for both Al free and Mg-Al alloys. To achieve this goal, the grain refining mechanisms of zirconium in cast magnesium alloys have been extensively studied and well covered in the literature [11, 23]. In this review, in addition to revisiting and summarising the remarkable milestones of grain refinement in Mg alloys, such as the role of Zr in grain refinement (See subsection 3.1.2), the most recently developed grain refiners, research progress in understanding the mechanisms of grain refinement in cast Mg-Al based alloys will be discussed in more details. This includes the new potent nucleants, solute element effects on grain refinement and different grain refining theories and models that were not fully covered in previous review papers.

2. Grain refinement theories and models for cast metals

2.1 Theoretical considerations in grain refinement of cast metals

For many years, heterogeneous nucleation [24] had been considered as the only cause of grain refinement in cast metals [25]. This is because more nucleation sites presented in the melt (nucleants) lead to more, small, equiaxed grains after solidification. However, the heterogeneous nucleation paradigm failed to propose a clear understanding of grain refinement in some alloy systems, such as Al-Ti-B master alloy in aluminium. In 1993, Johnsson [26] claimed that not only the nucleation event is the most dominant, but also the amount of solutes (segregating) quantified by the growth restriction factor (GRF) plays a major role in the grain refinement process. This paradigm has now been widely accepted due to its success in explaining a number of phenomena of grain refinement behaviours in many systems, such as Ca in AZ91 [27], as well as titanium and titanium boride in aluminium alloys [28], Ti [29] and Al–4Ti–5B [30] master alloy in AZ31 alloy and Zr in pure Mg.

Taking the potency of nucleants into consideration, it is well accepted that a potent nucleant always corresponds to the occurrence of nucleation with a low critical supercooling ($\Delta T_{n}$). In other words, the lower the $\Delta T_{n}$ is, the higher potency of the nucleant. The currently available theories,
proposed to model the potency of a nucleant, can be divided into two groups. One group rests on the hypothesis that a potent nucleant should have good crystallographic matching with the host matrix in order to minimize the interfacial energy between the nuclei and the matrix. This group includes the Turnbull and Vonnegut model [31], the Bramfitt model [32] and the edge-to-edge matching model [33]. The other group, focuses on the particle size of the inoculants, and believes that a potent nucleant should have a particle size larger than a critical threshold otherwise the nucleation cannot process irreversibly [34]. This is called the free growth model. On the other hand, the role of solute elements in grain refinement was argued to be very dominant. This argument was built on three main reasons. First, segregation of the solutes restrict the growth of previously formed grains giving more time for new grains to form [35]. Second, the segregation produces constitutional supercooling zone at the front of the solid liquid interface. This constitutional supercooling zone enhances the nucleants to nucleate new grains ahead of the growing interface, and therefore inhabit the growth of the existing grain. Third, the newly formed grains can also restrict the growth of the early formed grains producing the required equiaxed grains.

Recently, StJohn and co-workers [36] proposed a different mechanism to explain the combined effects of nucleating and solute elements on the size of the resulted grains. It is termed as the interdependence theory, describing the contribution of secondary nucleation within the constitutional supercooling zone to the reduction of as cast grain size. The principle of the interdependence theory has widely been accepted. However, the predicted grain sizes for cast aluminium alloys deviates a lot from the experimental results. The lack of accurate thermodynamic and kinetic data of solidification is possibly responsible for the inaccurate predictions. In the following section, the currently available grain refinement models/theories will be briefly discussed.

2.2 Models used for evaluating potency of inoculants based on crystallographic matching

To facilitate heterogeneous nucleation, a valid inoculant must fulfil two essential conditions. They are, (1) there is no chemical reaction between the inoculant and the molten alloy; and (2) the molten alloy has low wetting angle on the inoculant. In addition, in terms of the classic heterogeneous nucleation theory, to obtain higher nucleation rate and therefore improve the grain refining efficiency, it also requires low interfacial energy between the inoculant and the newly formed nucleus. Generally, there are number of factors affecting the interfacial energy [32]. These include crystallographic matching, electronegativity difference between inoculant and solid nucleants, size of the nucleants and etc. While full description of the interfacial energy is rather complicated, crystallographic matching has commonly been considered as a major factor that dominates the potency of inoculants, and the critical supercooling, ΔTn, required for heterogeneous nucleation to occur. To correlate the crystallography and the grain refining efficiency, various
crystallographic models have been proposed. The three most commonly used models are briefly reviewed as follows:

In 1952, Turnbull and Vonnegut [31] firstly noticed the importance of crystallography in grain refinement and proposed an empirical parabolic dependence model correlating the critical supercooling for nucleation ($\Delta T_n$) and the lattice disregistry parameter ($\delta$). It was reported that $\Delta T_n$ can be calculated using equation (1) [31]:

$$\Delta T_n = \left( \frac{c}{\Delta S_v} \right) \delta^2$$

where $c$ is the concentration of the solute and $\Delta S_v$ is the entropy difference (per unit volume) between the inoculant and the nucleus formed on it and the lattice disregistry $\delta$ can be calculated using the equation (2).

$$\delta = \frac{\Delta a}{a_o}$$

where $\Delta a$ is the difference in lattice parameters between the low index planes of the inoculant and the nucleus and $a_o$ is the lattice parameter in low index plane of the nucleus [31]. From equation (2), it can be seen that $\Delta T_n$ is proportional to $\delta^2$.

In this model, a potent inoculant should have a lattice disregistry factor of $\delta \leq 0.005$ to 0.015 [31]. The Turnbull and Vonnegut model is simple but limited to nuclei/inoculant systems that have the same atomic configuration on particular low index planes. As a result, little attentions have been paid on this crystallographic criteria until a modified version proposed by Bramfitt in 1970 [32]. The Bramfitt model is usually known as the disregistry model or the plane to plane matching (P2PM) model. The major change made by Bramfitt is redefinition of $\delta$ from linear disregistry to planner disregistry. By introducing a new parameter, the lattice disregistry could be expressed by equation (3) as follows:

$$\delta_{(hkl)}^{(nm)} = \Sigma_{j=1}^{2} \frac{\Delta a_{(hkl)}}{a_{(hkl)}} \times 100$$

where $n$ and $s$ denote the nucleus and the inoculant/substrate respectively; $(hkl)$ is a low index plane, $[uvw]$ is a low index direction on the $(hkl)$, $\theta$ is the angle between a pair of adjacent low index directions on the $(hkl)$.

Based on broad investigations for a relation between $\Delta T_n$ and $\delta$ on a number of inoculants in liquid iron, Bramfitt set up a lattice disregistry criterion of 12%, below which the inoculants are considered as potent nucleants [32]. This model has been used to explain the grain refining efficiency of a number of nucleants in light metals. This includes TiB$_2$ in an AZ31 alloy [29], AIC
and MgO in Mg-Al alloys [37-39]. Unfortunately, none of these refiners has grain refining efficiency as high as Zr in non-Al-containing Mg alloys and as TiB₂ or Al₃Ti in Al alloys.

The most recent crystallographic model that has been successfully used in interpreting the grain refining efficiency of successful grain refiners is the edge-to-edge matching (E2EM) model [33, 40-44]. The E2EM model was originally developed for understanding and predicting crystallographic features of diffusional phase transformations in solids. It combines criteria of interatomic spacing misfit, \( f_r \), between a pair of closed-packed rows and interplanar spacing mismatch, \( f_d \), between a pair of closed-packed planes that contain the rows. The major difference of the E2EM model from the Bramfitt model (P2PM) is that the E2EM model examines the matching at atomic scale, while the P2PM model uses lattice matching. For simple crystal system, the two models may lead to similar results. However, for more complicated crystal systems, the E2EM model is more accurate because, in real situation, it is the atoms to match across the interface rather than the lattice points. Thus, the E2EM model has an advantage over other crystallographic model that it can deal with more complicated systems where nucleus and nucleant are of significant difference in crystal structures and/or spacing between adjacent lattice points; while Bramfitt’s model loses its capacity/validity in this case.

Based on extensive examinations of crystallographic features, including orientation relationships and habit planes in various nucleants/matrix systems in Mg-Al and Al alloys, and in large number of diffusional phase transformations in solids, an empirical threshold for forming a semi-coherent or coherent interface between two crystals was proposed. It is \( f_r < 10\% \) and \( f_d < 10\% \) [41, 45]. This manes that for any crystalline particle in a liquid metal to be an effective nucleant the interface formed between this particle and the solid metal nucleated on it must be either coherent or semi-coherent. The essential condition to form such interface is that both \( f_r < 10\% \) and \( f_d < 10\% \).

The E2EM model has been successful in interpreting the heterogeneous nucleation behaviour of particles that were found at centres regions of refined grains [46-49]. Based on the E2EM calculation, Zhang et al. [40, 49-52] successfully predicted the relative grain refining efficiency of some previously known grain refiners in cast Al and Mg-Al alloys. It indicated that the order of grain refining efficiency for Mg-Al cast alloys is Al₂CO > Al₁C₃ > Al₆(Mn,Fe)₅, and it is Al₃Ti > TiC > TiB₂ for Al cast alloys. These predictions are fully consistent with experimental results [18, 40, 42-44, 53] regardless their thermal stability. In addition, the E2EM model has also been successfully used to develop new grain refiners for Mg-Al based alloys, such as ZnO, Al₂Y and AlN [54-57] (refer to Section 3.2.2.2 for more details).

### 2.3 Inoculant particle size effect – the free growth model
In addition to interfacial structure, Greer et al. [34] indicated that the size of the nucleants also significantly affect the heterogeneous nucleation rate, varying the gain refining efficiency. Greer proposed that the critical condition for a particle in the liquid metal to promote heterogeneous nucleation is \( d \geq 2r^* \), where \( d \) is the diameter of the nucleant and \( r^* \) is the critical radius of a nucleus, beyond which the nucleation can occur. This is termed as the free growth model, which correlates the critical supercooling with the size of the particle (nucleant) by the equation:

\[
\Delta T_n = \frac{4 \sigma_{Sl}}{\Delta h_d \cdot d_p}
\]

where \( \sigma_{Sl} \) is the solid-liquid interface energy, \( \Delta h_d \) is the entropy of fusion per unit volume and \( d_p \) is the diameter of the particle (assuming it is spherical) [34]. From equation (4), it can be seen that increasing the particle size can effectively reduce \( \Delta T_n \). Hence, large particles have higher potency to act as heterogeneous nucleation sites. The free growth model succeeded in explanation of the small \( \Delta T_n \) measured when Al alloys were refined by TiB2 (2–5 \( \mu \)m) [58] and when Zr (1–5 \( \mu \)m) and SiC were added to refine Al free Mg and AZ31 alloys, respectively [59, 60]. However, due to the lack of \( \sigma_{Sl} \) and \( \Delta h_d \) values for most substances, this model can only be used to qualitatively understand some phenomena of grain refinement in most cases.

### 2.4 The effect of solute elements on Grain refinement of cast metals

The role of solutes in grain refinement has been extensively discussed in the literature [11, 23, 25, 28, 34, 61]. More details about this paradigm can be found elsewhere [11, 25, 28, 62, 63]. It is accepted that the segregation of elements plays a major role in grain refinement. The key points of this solute paradigm can be summarized as follows:

The main hypothesis is the constitutional supercooling (CS), \( \Delta T_c \), resulting from the solute element segregation ahead of the growing dendrite/grain. This constitutional supercooling suppresses the growth of the dendrite/grain through promoting consequent nucleation when \( \Delta T_c \) is greater than \( \Delta T_n \) in the CS zone. In order to describe the impact of CS on the as-cast grain size, a “growth restriction factor” (GRF), or Q-value, is widely used. This term measures the rate of establishing the CS zone. Normally, high Q-value corresponds to high rate in establishment of the CS zone, resulting in smaller grains. In a binary system, the GRF can be simply expressed as:

\[
Q = m C_0 \cdot (k-1)
\]

where \( m \) is the slope of the liquidus line, \( C_0 \) is the initial composition of the alloy, and \( k \) is the equilibrium partition coefficient for element [11, 61-63]. Larger Q value indicates higher tendency of the solute to build up CS ahead of the growing dendrite/grain and higher possibility to produce smaller grains. The Q values of some common solute elements used in Mg alloys were provided in previous review papers [11, 23]. However, Q-values for less common solutes as micro-alloying
elements were not available in the literature. In order to provide a comprehensive guidance for development of new grain refiners, the Q-values of these solutes have been calculated by the present authors and are listed in Table 1. It is worth mentioning that these data are based on unit concentration at \( C_0 = 1 \) wt.% as presented in references [11, 23]. It should be emphasised that in real alloy systems, the actual Q values rely on the solute concentration, which in turn affects the grain refining efficiency. For comparison, the Q-values of the reported solute elements were also listed in Table 2. One can find that they are in a good agreement with those published in references [11, 23]. It should be noted that equation (5) is only valid to calculate Q values in a binary system. For alloys containing more than one element, the Q-values have to be calculated using the partial differential equation (6) [63].

\[
Q_{\text{true}} = \left( \frac{\partial (\Delta T_{\text{dep}})}{\partial f_{\text{S}}} \right)_{f_{\text{S}}=0}
\]

(6)
Table 1: Q-values of possible alloying elements used in Mg alloys at $C_0 = 1.0\text{wt}\%$ for binary systems.

<table>
<thead>
<tr>
<th>Element</th>
<th>m</th>
<th>K</th>
<th>$Q = m(K-1)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>-6.878</td>
<td>0</td>
<td>6.878</td>
</tr>
<tr>
<td>Pd</td>
<td>-4.07</td>
<td>0</td>
<td>4.07</td>
</tr>
<tr>
<td>Nd</td>
<td>-3.557</td>
<td>0</td>
<td>3.557</td>
</tr>
<tr>
<td>Co</td>
<td>-3.178</td>
<td>0</td>
<td>3.178</td>
</tr>
<tr>
<td>Sm</td>
<td>-3.4</td>
<td>0.135</td>
<td>2.943</td>
</tr>
<tr>
<td>Pr</td>
<td>-2.909</td>
<td>0</td>
<td>2.909</td>
</tr>
<tr>
<td>La</td>
<td>-2.895</td>
<td>0</td>
<td>2.895</td>
</tr>
<tr>
<td>Yb</td>
<td>-3.098</td>
<td>0.133</td>
<td>2.685</td>
</tr>
<tr>
<td>Ag</td>
<td>-4.217</td>
<td>0.366</td>
<td>2.675</td>
</tr>
<tr>
<td>Cd</td>
<td>-2.644</td>
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<td>2.644</td>
</tr>
<tr>
<td>Hg</td>
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<td>0.174</td>
<td>2.602</td>
</tr>
<tr>
<td>Eu</td>
<td>-2.49</td>
<td>0</td>
<td>2.49</td>
</tr>
<tr>
<td>Tb</td>
<td>-2.99</td>
<td>0.306</td>
<td>2.073</td>
</tr>
<tr>
<td>Li</td>
<td>-7.52</td>
<td>0.73</td>
<td>2.034</td>
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<tr>
<td>Au</td>
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</tr>
<tr>
<td>Ce</td>
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<td>1.725</td>
</tr>
<tr>
<td>Ir</td>
<td>-1.647</td>
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<td>1.647</td>
</tr>
<tr>
<td>Bi</td>
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<td>0.145</td>
<td>1.551</td>
</tr>
<tr>
<td>Ba</td>
<td>-1.169</td>
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<td>1.169</td>
</tr>
<tr>
<td>Gd</td>
<td>-2.595</td>
<td>0.605</td>
<td>1.025</td>
</tr>
<tr>
<td>Ho</td>
<td>-2.196</td>
<td>0.608</td>
<td>0.86</td>
</tr>
<tr>
<td>Dy</td>
<td>-2.349</td>
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<td>Tl</td>
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<tr>
<td>Tm</td>
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<td>0.557</td>
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<tr>
<td>Er</td>
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<tr>
<td>In</td>
<td>-2.681</td>
<td>0.864</td>
<td>0.363</td>
</tr>
<tr>
<td>Lu</td>
<td>-0.68</td>
<td>0.82</td>
<td>0.123</td>
</tr>
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</table>
### Table 2  Q-values for solute elements reported previously in Ref [11]

<table>
<thead>
<tr>
<th>Element</th>
<th>$m$ (K-1) calculated presently</th>
<th>$m$ (K-1) reported in Ref [11]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>52.68</td>
<td>52.56</td>
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<tr>
<td>Zr</td>
<td>30.24</td>
<td>38.29</td>
</tr>
<tr>
<td>Ca</td>
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</tr>
<tr>
<td>Si</td>
<td>9.42</td>
<td>9.25</td>
</tr>
<tr>
<td>Ni</td>
<td>6.053</td>
<td>6.13</td>
</tr>
<tr>
<td>Zn</td>
<td>5.003</td>
<td>5.31</td>
</tr>
<tr>
<td>Cu</td>
<td>7.402</td>
<td>5.28</td>
</tr>
<tr>
<td>Ge</td>
<td>4.778</td>
<td>4.41</td>
</tr>
<tr>
<td>Al</td>
<td>4.26</td>
<td>4.32</td>
</tr>
<tr>
<td>Sr</td>
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<td>3.51</td>
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<tr>
<td>Ce</td>
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<td>2.74</td>
</tr>
<tr>
<td>Sc</td>
<td>2.058</td>
<td>2.61</td>
</tr>
<tr>
<td>Yb</td>
<td>2.68</td>
<td>2.53</td>
</tr>
<tr>
<td>Y</td>
<td>1.624</td>
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</tr>
<tr>
<td>Sn</td>
<td>1.446</td>
<td>1.47</td>
</tr>
<tr>
<td>Pb</td>
<td>1.002</td>
<td>1.03</td>
</tr>
<tr>
<td>Sb</td>
<td>0.69</td>
<td>0.53</td>
</tr>
<tr>
<td>Mn</td>
<td>0.038</td>
<td>0.15</td>
</tr>
<tr>
<td>Ti (Ref. [30])</td>
<td>-</td>
<td>59500</td>
</tr>
</tbody>
</table>

### 2.5 The interdependence theory

In order to integrate the effects of nucleants and solutes, StJohn and co-workers [36] proposed an analytical model to describe the dependence of grain size on several key factors. It is assumed that grain formation is resulted from the interdependence between the nucleation and growth actions related to the surrounding environment alloy chemistry. The theory is based on the dependence of the as cast grain size on three major terms, as shown in Figure 1 [36]. These terms are quantified by: (i) the size of the previously nucleated grain ($x_{cs}$), is big enough to develop a sufficient constitutional supersupercooling (CS) zone for new nucleation event to occur; (ii) the distance ($x'_{dl}$) from the solid/liquid interface to the point where the CS is sufficient to nucleate a new grain (this region is called nucleation-free zone); and (iii) the distance ($x_{sd}$) from the
nucleation-free zone to the next most potent nucleating site where a new nucleation event can take place. Figure 1 illustrates the stages of nucleation according to the interdependence theory. The growing grain is represented by the circle on the top left of the diagram, the nucleant for the formation of a grain is denoted by a dot on the top right. According to the free growth model, the exponential curve represents the relationship between the nucleation supercooling ($\Delta T_n$) and the average particle spacing ($S_d$). $X_{cs}$ is the minimum distance required for the previously formed grain to grow so that a minimum constitutional supercooling, $\Delta T_n$-min, can form to promote the nucleation of the “new” grain on the nucleant denoted by the dot. The difference between the solid and dashed arcs marked by $t_1$ and $t_2$ denote the size of the growing grain at $t_1$ and $t_2$ times, respectively. At $t_1$ the grain was not big enough to create a CS zone at front of it to enable a “new” nucleation event to take place. But, at $t_2$ the bigger growing grain produced higher solute concentration that resulted in sufficient CS to promote “new” nucleation occurring. Hence, the distance between $X_{cs}$ and $X_{n zf}$ is the nucleation free zone, where no new nucleation occurs when the growing grain grew from the position at $t_1$ to position at $t_2$. Once the growing grain grew over $t_2$ time, the next (“new”) nucleation event takes place within the CS zone when the two curves ($\Delta T_n$-min and $\Delta T_n$-$S_d$) overlap. This implies that sufficient supercooling is presented to enable the next or “new” grain forms on the existing nucleant at point $X_{gs}$. The formation of this “new” grain inhabits the previously growing grain to further growth, leading to grain refinement.

![Figure 1: Schematic drawing for the nucleation process as proposed by the interdependence theory](image)

After extensive experimental investigations and theoretical calculations on large number of aluminium [64] and magnesium [65] systems; the latest version of the interdependence theory reported in 2011 [36] is represented in the equation

$$d_{gz} = x_{cz} + x_{d1} + x_{d2}$$

(7)
where $d_{gs}$ is the average grain size. Not only can this theory provide theoretical guidance to future work in predicting grain size of cast alloys, it also can be used to answer some questions associated with grain refinement, such as why only a minor fraction of the inoculant particles added into the melt can act as nucleation sites? However, this theory, also, has a few limitations. For example, the grain size predicted using Equation (7) varies in large range because of the inaccuracy, or insufficiency, of thermodynamic and diffusion data used in the calculation. The theory also cannot tell what type and size of particles are more effective to facilitate the heterogeneous nucleation and which solute can be added to create the CS with smaller nucleation-free zone. Therefore, the interdependence theory must be used together with other theories/models in order to develop new and more effective grain refinement processes for cast metals.

3. Effect of solute and/or potent nucleants addition on grain refinement of cast Mg alloys

In the last decade, based on the available theories/models of grain refinement developed in cast Al alloys, the effect of different alloying elements on grain refinement of cast Mg alloys has been studied, and a number of new grain refiners have been developed. In this section, the actual roles of different solutes, inoculants and the grain refiners in cast Mg alloys are reviewed.

3.1 The effect of solute elements on grain refinement of cast Mg alloys

The solute elements will be discussed in a descending order according to their Q values in Mg. Some elements, such as calcium and manganese, were discussed in a recent review paper by StJohn et al. [19]. This review highlights the latest findings for each element and some controversies are summarized.
3.1.1 Titanium and its grain refinement efficiency in magnesium

It has been approved that titanium is a crucial element in grain refinement of aluminium alloys. Al-Ti-B master alloys have been widely used in industries to produce high quality cast Al alloy products [25]. However, in magnesium alloys, due to the very limited solid solubility of titanium in magnesium, addition of titanium is considerably hard [66, 67]. Hence, there is significant discrepancy in the literature on the segregation power of solute Ti in Mg, because of the uncertainty about the liquidus and solidus lines at the Mg-rich side in the Mg-Ti binary phase diagram [67]. In 2005, Lu et al. [68] reported the Q value of titanium, in Mg-Ti system, is $Q_{Ti} = 6591.26$ k. Two years later, Wang et al. [30] calculated value of $Q_{Ti} = 59500$ k. Both values are 4 orders of magnitude higher than that of zirconium in Mg [11]. Thus, it was expected that Ti would have a very high grain refining efficiency for cast Mg alloys. But unfortunately, the study of titanium for either Al-free or Mg-Al alloys is scarce [21, 30]. The major challenge might lie, as mentioned above, in the fact that addition of titanium into liquid Mg is extremely hard [66, 67].

The reported results in literature are contradictive. Because of the difficulty of dissolving Ti into Mg alloy melts, Al-based Ti master alloy was used [21, 30, 69-73] in laboratories. Recent experimental work [70, 71, 73] showed almost no change in the grain sizes of as cast Mg alloys with $0.01 \sim 0.8$wt%Ti additions. Lee even [21] found grain coarsening in AZ91 alloy after titanium addition. But, Wang et al. [30] reported a noticeable grain refinement with titanium addition to AZ31 alloys. The major difference between Lee’s work [21] and Wang and co-workers’ work [30] was the content of Ti added to the melt. Addition of 0.01 wt.% Ti effectively refined the grains [30], but addition of 0.1 \sim 0.8$ wt.% Ti led to grain coarsening [21]. Wang et al. [30] also studied the effect of cooling rate on the grain refinement behaviour with Ti addition. It was reported that, at fixed composition, the grain size reduced with increasing the cooling rate from 3 to 6 K/sec then grain coarsening occurred when the cooling rate was further increased to 10 K/sec [30]. This is an abnormal phenomenon. Unfortunately, there is no further discussion. Based on the effect of titanium as a solute element with strong ability to segregate ahead of the solid/liquid (S/L) interface, a comprehensive discussion was presented by Wang et al. [30]. In this discussion, the effects of both peritectic reaction and Ti solute were considered as the major causes of grain refinement in an AZ31 alloy. The mechanical properties were also correlated with the final grain sizes in the alloys with various Ti additions. However, this discussion did not taken other factors into account. These factors include the Ti-Al intermetallic compounds formed in the melt, which promote heterogeneous nucleation. A patent granted in 2003 [74] described a grain refinement method using mixed powders of selected elements and compounds, including titanium, as grain refiner and
considered that the heterogeneous nucleation resulted in the grain refinement. Another recent patent [72] reported grain refinement of Mg alloys through addition of Al-Ti-Zr-C master alloy and considered that heterogeneous nucleation of α-Mg on Ti compound particles was responsible for the refined grains. The only work found supporting Wang and co-worker’s conclusion is an American patent, which was granted in 2007 [75] and updated in 2011 [69], used titanium as a grain refiner for AZ31 alloys. It was claimed that the grain size can be reduced by 90% compared to the non-refined AZ31.

Most recently, Yang et al. [76] reported that the addition of 0.1–0.3 wt.% Ti to Mg–3Sn–2Sr alloy resulted in improving the tensile and creep resistance. However, the grain refining efficiency was not very remarkable. But, after adding of 0.3 wt.% Ti, the grain size was reduced by ≈ 65% relative to the original grain size without Ti addition. No explanations were provided.

The research on the effect of titanium solute on grain refinement of Mg alloys is very limited. Due to the high value of m(k-1) of Ti in Mg-Ti binary system, Ti should have high potential to refine the grains of cast Mg alloys. However, because the solid solubility of Ti in Mg is negligible (almost zero), the actual Q value of Ti is expected to be very low. Hence, the solute effect of Ti on grain refinement of cast Mg alloys could be very marginal. However, if proper Ti-containing master alloys can is developed to provide sufficient and effective heterogeneous nucleation sites in Mg alloy melts, promising grain refining results could be obtained, particularly for Mg-Al based alloys. This requires further research to be conducted on this topic.

### 3.1.2 Zirconium has the best known grain refining efficiency with magnesium

With the high GRF (Q = 38.29 K [11]) and resembled crystal structure with Mg, zirconium has been reported as the most successful and effective grain refiner, currently known, for magnesium. It has been widely accepted that the most effective addition method of zirconium to molten magnesium is by using Mg-Zr master alloy. In 1945, the first commercially used Zr master alloy was produced and known as Zirmax [16]. But, it has three issues in industry applications. (1) High alloying temperature (780°C) is required to completely melt and dissolve the master alloy. (2) As Zr is very hard to dissolve in Mg melt, special mixing operation has to be used in the addition process; and (3) as a result of (2), Zr particles tend to settle to bottom of the crucible, leading to grain size inhomogeneity of castings. After revisiting the use of Zirmax master alloy, Qian et al. [77, 78] optimized the casting conditions to use this master alloy in Mg. They reported that within a temperature range of 680-780°C, two minutes stirring can essentially fully dissolve the master alloy in Mg melt. However, this method is not practical in industry operation. Finally, unlike the Al-Ti-B master alloy used for refining Al alloys, to achieve effective grain refining efficiency high level of
Zr addition up to 1wt % Zr is required. Hence, Zr is, in fact, an alloying element rather than a grain refiner. Such alloy is generally termed as Zr-containing Mg alloys.

When Mg-Zr master alloy is used in grain refinement of magnesium alloys, such as the ZK alloy [79], the most remarkable microstructural feature in Mg-Zr alloys is the Zr rich cores. These cores were reported in references [16, 80-82] and comprehensively studied by Qian and co-workers [80, 82]. Figure 2 (a) shows typical Zr rich particles and its presence in the centre regions of Mg grains. Before 1998, it was believed that only the dissolved zirconium contributes to grains refinement in Mg alloys [16, 83]. In 1998, Tamura et al. [84] reported that the undissolved Zr particles can also play a significant role in the grain refinement. This contention was further supported by Lee [21] and others [11, 77, 78, 85], who reported that undissolved Zr particles act as potent nucleants for α-Mg. Recently, it was reported that these nucleants have different geometrical shapes. Two different halo structures can be seen in Figure 2 (b) (spherical and dendritic) [80]. These halo shapes were studied by Qian et al. [85] and concluded that they are affected by the nature of the Zr nucleating particles. During solidification, when the melt contains high level of dissolved Zr (close to the solubility level), these halo structures grow in a spherical shape as a result of precipitation. On the other hand, when the level of undissolved Zr is high (above the sold solubility limit), these structures grow as prone to dendritic.

Figure 2: a and b show the Zr rich cores in magnesium matrix surrounded by halos in different shapes according to the nature of the nucleant [80].

However, the undissolved Zr particles tend to settle down to the bottom of the crucible due to the gravity and the density difference between the molten Mg and solid Zr particles. As a result, non-uniform grains from the top to the bottom of the ingot/casting are obtained [21]. Hence, stirring of the melt prior to pouring was proposed to be an essential process in order to produce homogeneous grain sizes when Mg-Zr master alloy is used [21, 77, 78, 85].

As the currently most effective grain refiner for Mg alloys, the high Q-value of Zr allows dissolved Zr to rapidly build up an effective CS zone ahead of the growing crystals, and the
undissolved Zr particles act as potent sites for heterogeneous nucleation. Hence, very significant grain refinement can be achieved with Zr addition to pure Mg. However, formation of intermetallic components with Al, Mn and Si restricted the use of Zr as a grain refiner in Mg alloys containing these elements.

3.1.3 The effect of calcium on grain refinement in Mg alloys

In the last decade, calcium has been extensively studied as a grain refiner in magnesium alloys. As can be seen in Table 1, Ca has a high Q-value of 11.94 [11], which comes in the second place after zirconium, indicating strong potential of Ca as a competitive grain refiner in Mg alloys, Mg-Al based alloys in particular. In addition, the low cost of calcium compared to zirconium is also attracting researchers’ interest.

Although the results reported by Emley [16] indicated no grain refinement effect when calcium was added to molten magnesium, St John et al. [19] considered calcium as an “effective” grain refiner for magnesium alloys. Moreover, a number of researchers reported a noticeable grain refinement efficiency when magnesium was inoculated using calcium. Some researchers reported moderate grain size reduction ratio (28.5-45 %) when Ca was added into the molten Mg [27, 86-88], while others reported 70 – 83 % reduction [23, 47, 89-94]. The latter can be considered very remarkable. The research on grain refinement through calcium inoculation can be categorized into two main groups. One focused on Al-free Mg alloys, and the other, on Mg-Al based alloys. Lee [23] and Shervin et al. [93] studied the effect of calcium addition on Al-free magnesium alloys using different purity of raw materials and different inoculation methods. Shervin et al. [93] used high purity Mg (99.9%) and added calcium to the melt using Mg-30%Ca master alloy while Lee [23] used commercial purity magnesium and calcium was added using Ca chips and granules in the alloying process. Both reported very significant grain refinement efficiency with 73% [23] and 81% [93] grain size reduction. The more remarkable grain refining efficiency reported by Shervin et al. [93] is attributed to the high purity materials used and the calcium addition content. Lee [23] considered that the role of solute elements, the effect of impurities and the in situ formed intermetallic compounds that might act as heterogeneous nucleation sites, all contribute to the grain refinement. But, Shervin and co-workers [93] only attributed the grain refining effect to the ability of solute calcium that restricts the growth of the grains without mentioning the effect of nucleating particles.

The reported grain refining efficiencies of Ca in Mg-Al systems also varies extremely from high [47, 89, 90, 92, 94] to moderate [27, 86-88]. Lee [23] and Peng et al. [88] considered that the purity of raw materials used in different work is the major cause for such variation in grain refining efficiency, which is supported by others [19, 21, 22]. Jiang et al.[47] examined the crystallography...
between Al$_2$Ca and Mg through theoretical calculation using the E2EM model and experimental determination. Due to the high consistency of the calculated results with the experimental ones, it was believed that the grain refinement of Ca addition is attributed to the high heterogeneous nucleation of Mg on Al$_2$Ca that in situ formed.

Another important phenomenon needs to be mentioned is the inconsistency of reported critical Ca addition levels to achieve maximum grain refining efficiency in Mg alloys. Some researchers [23, 86, 92] reported that Ca dramatically refined Mg grains when the addition was below 0.4 wt.% [14, 19] or 1 wt.% [92]. Further addition had no effect on grain size. Another group researchers [27, 47, 91] found that the grain size significantly decreased with Ca addition up to 0.8 wt% [47], 1.0 wt% [27], 2.0 wt% [91] and 4.0 wt% [93]. Further addition led to grain coarsening. Unfortunately, the causes of the coarsening are still not fully understood.

Based on the currently available reports, it is considered that calcium inoculation is a promising approach to grain refinement in cast Mg alloys, particularly in Mg-Al based alloys, provided the actual effect of Ca addition on grain refinement is comprehensively known and the mechanism is fully understood. Effective and low-cost master alloy (Mg-Ca-X) will be also welcome by Mg manufacturers due to its better compatibility with both Al-free and Al-containing Mg alloys. Comprehensive research work needs to be done to elaborate the effect of the solute together with the effect of potent nucleates. Finally, the effective range of calcium addition to achieve maximum grain refining efficiency needs to be clarified as well.

3.1.4 Grain refining effect of Silicon in Mg alloys:

With growth restriction factor of $Q = 9.25$ K [11], silicon was supposed to have strong segregation power in magnesium and therefore to significantly refine the grains of as cast Mg alloys. However, one of the major problems associated with Si addition is the formation of Mg$_2$Si intermetallic phase [95-99]. This phase was not only negatively affects the mechanical properties by acting as crack initiators, but also weakens the grain refining efficiency. In 1948, Nelson [100] reported that small amount of silicon addition into Mg alloys led to grain refinement, followed by grain coarsening with higher addition. Recently, Lee [21] reported that the critical addition level of Si for grain refinement in pure Mg is 0.15 wt.%, over which no further reduction in grain size was observed. The grain refining efficiency of Si can be strengthened through concurrent addition of other alloying elements. It was reported that addition of Sb [95] and Sr [98] to Mg-Al-Si alloys resulted in a noticeable grain refinement effect. Calcium addition to the same system was found to produce CaSi$_2$ particles, which were believed acting as heterogeneous nucleation sites [99, 101], promoting the grain refinement efficiency. In addition, silicon carbide (SiC) is also considered as an
effective grain refiner for Mg-Al based alloys, which will be discussed in more details in Section 3.2.1.

Because the reported growth restriction factor of Si in Mg alloys was calculated in terms of Mg-Si binary system, it could not give a full understanding for some of the reported results in the literature. In order to completely exploit the grain refining potency of Si in Mg alloys, the growth restriction factor of Si should be calculated in different ternary or even quaternary systems. Comprehensive understanding of the grain refining mechanisms of Si may lead to development of new and more effective grain refiner for Mg alloys.

3.1.5 Role of sodium in grain refinement of Mg alloys

The high chemical activity of sodium and its low solid solubility in magnesium (≈0.5 at.% [67]) could be the two main reasons for the lack of interest. In addition, no intermetallic phases have been observed when Na was added into molten Mg. However, based on the Mg-Na phase diagram, the Q value of sodium is ~ 6.87 K, which suggests that Na is a moderately effective solute element for grain refinement. Although Mendis et al. [102] found an increase in hardness after ageing of a Mg alloy prepared through addition of sodium to the pure Mg using Sn-11.8Na (at.%) master alloy, no grain refinement was observed [102]. Recently, Stanford et al. [103] reported a noticeable grain refinement effect by sodium addition to Mg-Sn-1Zn alloy. However, neither Stanford nor Mendis correlated the property improvement to grain refinement due to the solute effect of Na. Hence, the effect of Na on grain refinement in Mg alloys needs further studying in more details.

3.1.6 Using copper as a grain refiner for Mg alloys:

Copper inoculation in cast Mg was first reported by Nelson [100]. Grain refinement effect was observed in Mg-Cu alloys after superheating treatment but no detailed experimental data was presented. In addition to its reasonable growth restriction factor (5.28 K) [11], Emley [16], mentioned copper as a grain refining element for magnesium. However, this early work was not well followed up due to some potential issues as detailed below.

One major concern of adding copper to magnesium melt is its very low solid solubility [66, 67, 79]. In addition, copper reacts with magnesium forming Mg$_2$Cu intermetallic phase [66, 67, 104-107] which reduces the formability of the alloy. Corrosion resistance of Mg alloys is also weakened by addition of copper [66, 79, 108] due to the high corrosion rate of the alloy as “copper acts as active cathodic site for the reduction of water at the sacrifice of elemental magnesium” [79]. In 2002 and 2003 [104, 105] Hassan et al. used copper as a reinforcing material for pure magnesium
trying to improve the mechanical properties by producing new composites. Copper was added to into Mg in the form of multilayer sandwich, which was melted in the crucible at temperature of 750°C, followed by casting in argon gas ambient. A reduction of Cu particle size from 8 – 11 μm to ~ 1 μm was reported. It was found that copper particles uniformly distributed in the samples together with the in situ formed Mg₂Cu intermetallic phase in the centre region of the grains or on the grain boundaries. With copper addition, in Hassan and co-workers’ work, hardness, elasticity and tensile properties were improved with sacrificing the ductility. However, their discussion focused on copper particles and Mg₂Cu intermetallic phase effects, ignoring the effect of grain size on the mechanical properties. In 2006, Blawert et al. [108] reported the effect of Cu addition on the microstructure and corrosion resistance of AZ91 alloy. Grain size reduction (from 500 to 200 μm) was found with increasing Cu content up to 2 wt.% with decreasing corrosion resistance. Recently, Chen and co-workers [107] studied the effect of copper on damping capacity of Mg-1%Cu alloy. Pure Mg metal was firstly melted and the Mg-30wt%Cu master alloy was added at 770°C, followed by cooling down to 750°C, at which melt was cast into a mould preheated at 250°C under the protection of CO₂+SF₆ gas mixture. Remarkable grain refinement was found with grain size reduction from 291.5 μm to 28.5 μm at 3wt% Cu addition. Although Zhang et al. [106] found the similar grain refinement of Cu in Mg alloys, results were not well emphasised and discussed. In addition, concurrent addition of Cu and Mn varied the grain refining efficiency and reduced the grain size from 201 μm to 66 μm but, no discussions were provided. Thus, the grain refinement mechanism of Cu addition is still beyond full understanding. In addition to the growth restriction factor, potency of the nucleating particles that promote the heterogeneous nucleation also needs to be taken into consideration [11, 19, 20, 23, 25, 28, 109]. Further and more comprehensive research on the effect of Cu addition on grain refinement should be conducted in order to give a better understanding for this system.

3.1.7 The effect of silver, tin and cobalt on grain refinement in Mg alloys.

Relatively, not much work has been done investigating the influence of silver, cobalt and tin on grain refinement of magnesium alloys. In 1966, Emley [16] reported the dependency of smaller grains, formed, in cast magnesium upon existence of silver or tin. However, as the reported Q values of these three elements are 2.675, 3.178 and 1.47 K for Ag, Co and Sn [11] respectively. It is believed that, most likely, their ability to act as solutes in Mg grain refinement is not really promising.

Gusieva et al. [110] studied the effect of trace silver addition on the microstructure as well as the mechanical and chemical properties of an AZ91 alloy. It was found that addition level of 0.12wt.% Ag converted the conventional lamellar Mg₁₇Al₁₂ phase into a “swirl-like” lamellar
morphology [110]. Mg₄Ag intermetallic phase was also identified [110] which was considered to increase, both, the hardness and electrochemical corrosion rate [110] even though the actual mechanism, behind this, is yet unclear.

Tin, is a typical alloying element in magnesium alloys and has been widely studied, as tin improves creep resistance, particularly at higher temperatures [102, 111-114]. Relatively, there are fewer reports discussing whether tin can refine the grains of cast Mg alloys compared to those reporting the effect of tin on Mg creep resistance. Rzychon et al. [114] claimed that addition of tin had a positive impact on grain refinement by promoting heterogeneous nucleation on CaMgSn particles. Also, Mendis et al. [102] reported that when Sn-Na master alloy was added to pure magnesium, grain size reduction was observed. These results supplement the experimental findings reported in reference [114], when grain size reduction was reported due to the addition of Sr with Ca, Al and Mn. However, it is believed that the presence of other elements complicate the understanding of, the actual, grain refining role of Sr [114]. In addition, tin has also been added in Al-free [111, 112] and Al-containing [112, 113] Mg alloys. Although creep resistance was increased, the effect on grain refinement was not discussed in these references.

Cobalt was added in magnesium by Klose et al. [115, 116], for development of sensor material, using both cobalt powder [116] and Mg-40vol.% Co billets produced by compressing both metals powders [115]. Although the variation of grain size was not discussed, noticeable grain reduction can be observed in Figures 4 and 1 in [115] and [116] respectively. No more papers in the literature could be found discussing the effect of Cobalt addition on magnesium alloys.

Due to the lack of research in this area, the actual effects of additions of silver, cobalt and tin on both grain refinement and properties of Mg alloys are far beyond understanding. Further studies on this topic may lead to development of not only new alloys, but also new grain refining process.

3.1.8 The role of Manganese in grain refinement of Mg alloys

Manganese is one of a few peritectic-forming elements with Mg. Thus, although the growth restriction factor of manganese in the Mg-Mn system is only 0.15 K [11], which is considerably low, Mn still attracts researchers’ interests in inoculation treatment of Mg alloys. In 1961, an American patent [117] reported that 0.2% Mn addition to AZ91 and AZ92 alloys led to grain refinement, which was attributed to a superheating reaction. Moreover, in the last decade, a number of researchers successfully refined Mg-Al grains using Mn [52, 118-120]. But, grain coarsening with Mn addition was also reported [52, 120]. It has been noticed that Mn can act as a grain refiner for Mg-Al alloys only when the superheating method is applied. Even under the superheating conditions, excess addition of Mn or holding the melt for long time at high temperature causes grain coarsening [52, 120]. These problems attracted the research community and many literatures were
found trying to explain the duplicated effect of Mn in Mg. As an explanation for grain coarsening results from excess Mn addition, Du et al. [52] assumed that with excess of Mn addition to the melt, aluminium content will decrease due to the formation of Al-Mn intermetallic. This leads to a reduction in the constitutional supercooling which is required for the nucleation process. Hence, no more nucleation events will take place and grain coarsening will occur. This hypothesis was not very convincing as it cannot explain the grain refining behaviour reported by Tamura et al. [121].

Considering the importance of superheating in Mg inoculation by Mn, two of the early hypotheses to explain the phenomenon were the temperature-solubility nucleation theory [100] and the temperature phase relationship model. The first theory tried to explain this behaviour by assuming that the Mn particles are too big for the nucleation event to happen at low temperatures and the superheating temperature is essential to break these big particles into smaller ones that are applicable to nucleate Mg. The other one relies on an assumption that manganese compounds with hexagonal crystal structure can act as potent nucleants, and these compounds will only be stable in the superheating temperature range. Both models were tested by Tamura et al. [121] when Mn was added to AZ91 using rapid solidification method. It was concluded that both theories are not valid to explain the Mn refining behaviour [121]. The temperature-solubility nucleation theory is not valid because the large Mn particles, which were supposed to be stable at superheating, completely disappeared at 690°C, which is very far from Mg superheating temperature. The temperature-phase relationship theory is not valid because no hexagonal manganese compounds were found in the samples after isothermally holding the melt at superheating temperature.

In the last decade, researchers tried to correlate the Mg-Al-Mn nucleation particle with the use of superheating to reveal the contradiction in this area. A number of researchers [46, 53] reported Al₅Mn₃ can act as potent nucleant for α-Mg. However, this claim was contradicted with the experimental findings by Laser et al. [118] who did not find Al₅Mn₃ particles in the grain refined samples, but it was presented in the coarsened grains. In 2005 and 2006, Cao and co-workers [119, 120] claimed that the metastable ε-AlMn phase, after proper addition of Mn, should act as potent sites for heterogeneous nucleation. However, holding the melt for long time at high temperatures will transform the metastable phase into stable Al₅Mn₃, which cannot act as potent nucleants and this may lead to grain coarsening. Cao’s hypothesis [119, 120] was successful in explaining the grain coarsening effect reported by Laser et al. [118] and Tamura et al. [121]. Recently, Cao et al. [122] proposed an alternative model to explain this phenomenon. They postulated that the potency of Al₄C₃ particles is the main reason underlying the grain refinement behaviour and the nucleants poisoning take place when Mn/Fe impurities coat the nucleants. As a solution, to avoid the poisoning effect, Cao et al. [122] suggested that heating the melt up to 800-900°C will remove the
impurities from the surface of Al₄C₃ and hence recover the potency of Al₄C₃ as the nucleation sites. Hence, Superheating is essential for Mn inoculation process. More recently, using the edge-to-edge matching (E2EM) crystallographic model, it was proved that ε-Al-Mn particles, which were proposed by Cao et al. [119, 120], are not as potent as τ-AlMn [45, 52]. Superheating the melt leads to formation of metastable ε-Al-Mn phase. Upon cooling the high temperature ε-Al-Mn particles partially transfer to τ-AlMn prior to solidification, which act as heterogeneous nucleation sites for α-Mg. Hence, small equiaxed grains form. These results were supplemented by the experimental finding reported by Du et al. who observed the presence of ε-Al-Mn in the centre of the grains, but the τ-AlMn phase could not be found unless superheating was applied [52].

As mentioned above, it could be said that the contradictory of Mn behaviour as a grain refiner in Mg-Mn alloys is not yet resolved. More research effort is needed to fully understand the role of Mn in Mg inoculation. A model explaining the manganese behaviour in Al-free Mg alloys is essential in understanding the mechanisms.

3.1.9 Effect of rare earth on grain refinement in Mg alloys

For decades, rare earth (RE) elements have attracted increasing interest in development of new magnesium alloys because RE-containing Mg alloys have remarkable creep resistance [123] and improved mechanical properties. Typical alloys include EZ33, WE43, WE54, ZE41, ZE63 and AE42 [79]. These alloys have been mainly used in aerospace applications [19] due to the high cost of rare earth elements.

Many RE elements exhibited good grain refinement effect in cast magnesium alloys. Addition of La, Pr and Ce to Al containing Mg [124] resulted in significant grain refinement. Tao et al. [124] considered that restriction of grains growth of segregated RE elements at front of growing liquid/solid interface is the main cause of the grain refinement. This hypothesis was based on the observation of RE-containing intermetallic phases on the grain boundaries of the cast alloy. Also, it was supported by Chia et al. [125] who added La, Ce and Nd to pure Mg and similar grain refining results were obtained.

3.2 The effect of potent nucleants on grain refinement in Mg alloys:

Even though the solute paradigm is widely regarded as the most dominant factor controlling the grain refinement process, some grain refining findings were awarded to the potent heterogeneous nucleation sites and the potency of the nucleants presented in the melt. Many trials have been done on various compounds to test their potency and investigate its grain refining effect in Mg alloys, particularly in Al-containing Mg alloys. In this section, the most popular nucleants for Mg-Al based alloys are reviewed.
3.2.1 Carbon inoculation:

Due to the high energy consumption involved in the superheating process, researchers are seeking an alternative approach to refine the grains of cast Mg-Al based alloys. Carbon inoculation, which was first reported in 1940 [16], is one of the most successful techniques. Carbon can be introduced to the melt in various forms, including master alloys, C₂Cl₆, Al₄C₃ particles and graphite powders [18, 37, 126-132]. Because carbon inoculation method is not effective with Al-free magnesium alloys [18, 133, 134], it is commonly considered that aluminium carbide plays the key role as the potent nucleant that dominate the grain refining behaviour in this process [18, 37]. But, Jin et al. [135] reported carbon segregation that may also contribute to grain refinement. Cao and co-worker [18] studied this hypothesis experimentally and concluded that the effect of potent nucleants is more dominant than the segregation in the carbon inoculation process. Moreover, existence of potent nucleants that promote heterogeneous nucleation is commonly considered as the main cause of the grain refinement. The major dispute, in this area, is the species of the potent nucleant particle.

Emley [16] reported that Al₄C₃ can act as a potent nucleant for α-Mg. This hypothesis was supplemented by other researchers [18, 131] who considered Al₂CO can also be the nucleant in addition to Al₄C₃. Based on the disregistry model, Lu et al. [37] found Al₄C₃ has higher potency than Al₂CO, and considered that the formation of Al₂CO is probably resulted from the reaction of Al₄C₃ with water during samples preparation. This claim was supported by other researchers [37, 127, 128]. In 2007, Kim et al. [129] reported Al₆(Mn,Fe)₅ to be more potent than Al₄C₃. Also in 2010, Du et al. [132] found Al-C-O-Fe rich particles in addition to Al-C-O in the centre of Mg grains and claimed that Fe has a positive effect on the potency of the nucleant, if it is introduced to the melt prior to carbon addition. But, these hypothesis were not supported by the E2EM calculations [50] as the atomic mismatch between Al₆(Mn,Fe)₅ and Mg is too high. In addition, the experimental results reported in [53] verified the low efficiency of Al₆(Mn,Fe)₅ as a potent nucleant for α-Mg. More recently, Al₂MgC₂ was reported to be more potent than Al₄C₃ in terms of the crystallographic matching [19, 136]. However, this hypothesis needs to be validated through comprehensive experimental work.

Silicon carbide (SiC) [60, 136, 137] is another potent nucleant that can form through carbon inoculation. However, SiC can be treated as a unique grain refiner due to the remarkable grain refining effect when added to Mg-Al alloys, containing less than 9 wt.% Al [137]. Despite SiC has never been theoretically validated as a potent nucleant, Easton et al. [97] explained the effect of SiC in a Mg-Al(-Mn) alloy in terms of the empirical relationship
where \( \%P \) is the particle addition rate in wt.\%, \( \Delta T_n \) is the nucleation supercooling, \( a \) and \( b \) are the intercept and gradient, respectively, when the grain size is plotted against \( 1/Q \) and \( Q \) is the solute content [138].

Although a number of carbides can act as valid heterogeneous nucleation sites leading to grain refining in Al-containing Mg alloys, none of them is as effective as Zr in Al-free Mg alloys. In order to develop more effective grain refining processes for this type of alloys, the mechanisms of grain refinement in cast metals need to be fully understood.

### 3.2.2 Other potent nucleants for cast Mg alloys

In addition to the carbides formed during carbon inoculation process, many other compounds have also been tested in promoting heterogeneous nucleation of Mg alloys. Most of these compounds exhibited more or less grain refining potency, but none of them met the standards for commercialization. These potent nucleants can be divided into two main categories. Nucleants in the first category were discovered based on experimental work (subsection 3.2.2.1), and the ones in category two were predicted through crystallographic calculations.

#### 3.2.2.1 Potent nucleants discovered based on experimental results

Borides, such as \( \text{ZrB}_2 \) particles, were found to be potent nucleants in pure Mg and Al-containing Mg alloys [139]. Small equiaxed grains were obtained when \( \sim 4 \mu \text{m} \) \( \text{ZrB}_2 \) particles were added into pure Mg [139]. The grain size was also reduced from \( \sim 450 \mu \text{m} \) to \( \sim 60 \mu \text{m} \), with 0.5 wt. \% \( \text{ZrB}_2 \) addition. In 2004, boron nitride was patented as a grain refiner for Al containing Mg in Germany [140] when a grain size of 60-120 \( \mu \text{m} \) was achieved. Two years later, in 2006, Wang and co-workers [29] studied the effect of Al-4Ti-5B master alloy, which is a typical commercial master alloy for inoculation treatment of Al alloys, on the grain refinement of AZ31. 90\% reduction in the grain size was obtained with 0.3 wt.\% Al-4Ti-5B master alloy addition to the melt. In terms of the Bramfitt model, Wang et al. [29] calculated the lattice disregistry (\( \delta \)) between TiB\(_2\) and \( \alpha\)-Mg and found it is \( \delta = 5.6 \). Hence, TiB\(_2\) was believed as a potent nucleant for \( \alpha\)-Mg nucleation. This result was further confirmed by Liu et al. [38], who found TiB\(_2\) particles in the central regions of Mg grains when Mg-TiB\(_2\) master alloy was added to AZ91.

Another potent compound was reported by Vidrich et al. [141] who mixed nanometre scaled TiN powder with AZ91 or AZ31 powders and pressed the mixtures into billets, which were then added to the melts of AZ91 or AZ31. 0.6 vol.\% TiN was obtained in the melt before gravity casting.
and no chemical reaction between TiN particles and the matrix was observed. Smaller grains were presented in the as-cast AZ91 than in AZ31, indicating that TiN particles were more potent with the higher Al content alloy. However, this conclusion is questionable as smaller grains in AZ91 alloy could be attributed to the higher content of Al. More recently, Fan et al. [46] successfully refined AZ91 grains using intensive melt shearing technique and \( \sim 40\% \) reduction in grain size was obtained in the sheared samples. Based on XRD results, Fan et al. [46] considered that the presence of MgO and Al\(_8\)Mn\(_5\) particles in the melts were responsible for the grain refinement. Fan and co-workers [46] calculated the atomic mismatch along the closely packed directions between \( \alpha \)-Mg and Al\(_8\)Mn\(_5\) and between \( \alpha \)-Mg and MgO, it was found that the mismatch of \( \alpha \)-Mg with MgO is 5.8\% and it was 17.8\% Al\(_8\)Mn\(_5\). Hence, MgO was considered a more effective nucleant than Al\(_8\)Mn\(_5\).

In 2010, Kim et al. [48] reported that MnCO\(_3\) has noticeable grain refinement effect in Mg-Al cast alloys [48]. The average grain size was reduced from \( \sim 480 \) to \( \sim 61 \mu\text{m} \) with 0.6wt\% MnCO\(_3\) addition to the melt. Based on the E2EM model, Kim et al. [48] found that both MgO and Al\(_4\)C\(_3\) have much lower interatomic misfit with \( \alpha \)-Mg than Al\(_8\)Mn\(_5\), and considered MgO and Al\(_4\)C\(_3\) as the potent nucleants for \( \alpha \)-Mg. However, from the HREM micrographs, Kim et al. [48] observed that Al\(_8\)Mn\(_5\) has a coherent and strong bond with \( \alpha \)-Mg phase, suggesting that this Al-Mn intermetallic may lead to the grain refinement. Moreover, it was believed that Al\(_4\)C\(_3\) will act as a heterogeneous nucleation sites for Al\(_8\)Mn\(_5\) (not \( \alpha \)-Mg) and hence, the grain refinement observed came from a duplex reaction. Kim et al. [48] used their experimental results reported in 2007 [129] to support this hypothesis. Nevertheless, experimental results from a more recent paper [53] contradicted with Kim’s hypothesis, supporting crystallographic predictions from the E2EM calculations reported in 2005 [50].

In addition to the increase in creep resistance and strength of Mg-Gd alloys [6, 7], addition of 0.8\% to 1.3\%, aluminium to Mg-10Gd alloy led to obvious grain size reduction [142]. Dai et al. [142] found Al\(_2\)Gd particles in the centres of the grains, indicating that Al\(_2\)Gd is an effective nucleant for \( \alpha \)-Mg. In addition, reproducible orientation relationships (ORs) between Al\(_2\)Gd and \( \alpha \)-Mg phase were also determined using electron diffraction in TEM [142], which further verifies the potency of Al\(_2\)Gd as an nucleant for \( \alpha \)-Mg nucleation. Similarly, Dai et al. [143] recently reported significant grain refinement with 0.6-1 wt.% Al addition to Mg-10Gd-3Y alloy. Al\(_2\)(Gd\(_{0.5}\)Y\(_{0.5}\)) particles were found at the centres of the grains and electron diffraction in TEM showed reproducible ORs between Al\(_2\)(Gd\(_{0.5}\)Y\(_{0.5}\)) and \( \alpha \)-Mg phase, evidencing the efficiency of these particles as active nucleants [143].

### 3.2.2.2 Potent nucleants designed using crystallographic models
Although heterogeneous nucleation on foreign particles depends on a number of factors, such as the wetting angle of the liquid metal on the solid particle, the particles size distribution, the shape of the particles and their chemical properties, crystallography remains as the only factor that has been well-understood and can be calculated. The matching between the host metal and nucleants has been widely used to explain the grain refining efficiency [48, 56, 66, 144-147] and to seek new nucleants. The E2EM model has been one of the most successful crystallographic models that are capable of predicting new nucleants for cast metals [40, 54-56].

In 2007, Fu et al. [56] reported that ZnO can act as a potent nucleant for α-Mg phase when added in powder form to pure magnesium. As ZnO has almost identical crystal structure to Mg, it was strongly believed that ZnO can well refine the as cast structure of Mg alloys. However, from the thermodynamic point of view, as ZnO can be rapidly reduced by Mg forming Zn + MgO, its grain refining efficiency was not as high as expected. Furthermore, another potent nucleant in Mg alloys that was discovered and verified by the E2EM calculation is AlN [54]. Fu et al. [54] reported the interatomic misfit along the matching directions and the interplanar mismatch between AlN and Mg to be 2.67 and 2.6 %, respectively. Thus, AlN was considered as an effective nucleant in Mg alloys. But, for some reasons that were not provided, the highest grain refining efficiency was only achieved at casting temperature of 765°C with 0.5 wt.% addition of AlN to Mg-3wt.% Al alloy. This is practically invalid due to the high casting temperature. Another successful example of the application of the E2EM model are Al2Ca [47] and hafnium carbide (HfC) [48]. The smallest interatomic misfit and d-value mismatch between α-Mg and Al2Ca is 2.1% and 1.6%, respectively. They are 2.4% and 5.1%, respectively between HfC and α-Mg[48]. The average grain size in Mg-3wt.% Al alloy was reduced 70% by 0.08% Al2Ca addition and 60% with 0.7 wt.% HfC addition.

One of the major successes of E2EM in Mg grain refinement and in predicting new potent nucleants is the Al2Y in Y-containing Mg alloys. Although Lee et al. [147] reported the effect of yttrium on grain size reduction of as cast AZ91 alloy in 1998, the role of Al2Y in grain refinement was not well recognized. Instead, it was believed that the Al2Y intermetallic enables the morphology change of Mg17Al12 phase from continuous to discontinuous. Grain coarsening was also reported when yttrium was added to Mg alloys containing more than 2wt%Al [148, 149]. More recently, Qiu and co-workers [57, 145, 146] have been successful in predicting the Al2Y phase as a potent nucleant based on crystallographic calculations using the E2EM model. Addition of 0.6-1.0 wt.% Al into Mg-10 wt.%Y alloy led to the grain reduction from 180 µm to 36 µm [57, 145, 146]. Unfortunately, no further research has been carried out investigating whether Al2Y is a valid nucleant in other Mg alloys.
As a conclusion, due to the complexity of mechanisms of grain refinement in cast metals, there are still lack of effective grain refiners, which should contain both potent nucleants to facilitate the heterogeneous nucleation and proper solutes that promote the establishment of constitutional supercooling, for Al-containing Mg alloys. At least at this stage, crystallographic calculation, such as using the E2EM model, remains a powerful tool to develop new grain refiners.

4. Summary:

There is no unique model has been developed that can be used to comprehensively explain phenomena associated with grain refinement in different cast alloys. The currently available heterogeneous nucleation and the solute paradigms, and the combined interdependency theory, help the research community to set the basic principles for grain refinement process. The growth restriction factor can be effectively used to identify potent solutes that possibly lead to effective grain refining efficiency. The current challenge is how to accurately calculate the growth restriction factor or Q-values of solutes in multiple alloying elements systems. Crystallographic models, such as the edge-to-edge matching model, have been widely used as an effective and useful tool to predict the grain refining potency of potent nucleants in Mg alloys. The presences of potent nucleants and solute with high GRF in a specified alloy system are essential to achieve satisfied grain refining efficiency. Development of more effective grain refiners or master alloys for both Al free and Al-Mg alloys can be achieved through identifying promising nucleants using one appropriate crystallographic matching model and through calculation of Q-values of potent solutes. In addition, other factors, such as the nucleant size, morphology and number density etc. in the master alloy, mush also be taken into account.

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2.3 **Update on the research progress of the topics mentioned in the review paper**

Grain refinement of magnesium alloys is a continuously active research topic. Since Paper 1 was published in 2015, a number of new articles on grain refinement of Mg alloys have been published. Although there was no revolutionary breakthrough in developing new grain refinement techniques and in understanding the mechanism of grain refinement of cast Mg alloys in the last two years, significant research progress has been made in understanding the effects of solutes in Mg based alloys and in identification of new grain refiners.

### 2.3.1 Effects of solutes on grain refinement of cast Mg alloys

The effects of calcium addition on the as-cast microstructure of Mg-Al based alloys were revisited recently in Nagasivamunis’ et al. work [18]. Grain refinement was found in all three base alloys, Mg-3Al, Mg-6Al and Mg-9Al, with Ca addition. While the grain refinement was suggested to be mainly due to the Ca solute affect. It was also reported that Ca contributed to enhancing the native nucleation by increasing the constitutional undercooling during solidification. Most recently, Xiaoping et al. [19] added Ca to Mg-Sm base alloy and found that the grain coarsening took place when the Ca addition was over a critical level. In fact, this is long-standing phenomenon, which cannot be fully understood. Larger grains were obtained at 1.5 wt.% Ca addition to Mg-0.4Sm base alloy. Grains were coarsened from 45 μm in the Mg-0.4Sm-1Ca alloy to 57 μm in the Mg-0.4Sm-1.5Ca alloy. Unfortunately, the causes of the coarsening were not reported in the study and could not be found anywhere in the literature.

Despite the controversial nature of manganese as a grain refiner in Mg-Mn alloys, one group of researchers added Mn into a Mg-4Zn-0.5Ca ternary base alloy for biological applications [20]. Results showed that addition of Mn led to significant grain refining. It was believed that Mn addition led to the increase in the number density of heterogeneous nucleation sites through decreasing the critical nucleus size. However, Mn addition into a quaternary alloy led to inconsistent results and for more reliable results, further study is needed.

In the last two years, research interest has been focused on studying the effects of RE elements in Mg-RE systems and Sm in particular [21-23]. Wang et al. reported that addition of Al into Mg-Sm base alloy led to a significant grain refinement [23]. This was highly likely due to the formation of Al-RE intermetallic compounds that were reported previously in Mg-Al-Y system. On the other hand, when 0.7 wt. % Sm was added to Mg-3wt.%Al base alloy, grain coarsening was reported [22]. But, with increasing the Sm content to 2.1 wt. %, the average grain size dramatically decreased. It has been claimed that lower contents addition of Sm led to poisoning of potent Al-Fe-
C-O particles, and hence, grain coarsening occurred [22]. With plenty of Sm in the melt, it is believed that the number density of potent Al$_2$Sm particles increased, which served as nucleants for $\alpha$-Mg, leading to grain refinement [22, 23].

### 2.3.2 Recently reported new grain refiners/nucleants for $\alpha$-Mg

Even though carbon inoculation has been one of the most popular approaches to grain refinement of Mg alloys, more effective inoculation treatment is needed for Mg-Al base alloys. In the past two decades, one of the major controversies is the effective nucleants during carbon inoculation of Mg-Al based alloys. This controversy has been clarified in the last two years by Bae et al. and Liu et al. Their results supported the hypotheses that Al$_4$C$_3$ is actually the valid and effective nucleant for $\alpha$-Mg rather than Al$_2$MgC$_2$ [24, 25]. Du and co-workers [26] reported that combining carbon inoculation with the addition of small amounts of Ca and Fe led to extraordinary grain refinement in a Mg-3.0wt.%Al base alloy. But, the phenomenon was not well-explained.

The majority publications on grain refinement of Mg alloys in the last two years focused on identification of new grain refiners that work for both Al-free and Mg-Al base alloys. Wang et al. [27] reported that the *in situ* formed ZrB$_2$ particles when Al-5Zr-1.1B master alloy was added into AZ91D melt led to refining the grains of the base alloy to a final average diameter of 45 $\mu$m. They also found other borides could also refine the Mg grains [27, 28]. Another study [29] was found addition of Al–5Ti–1B master alloy led to grain refining of an AZ91E alloy.

As mentioned in Paper 1, Ti solubility in Mg is almost zero. Hence, Ti based inoculants have been of a high interest by researchers for two reasons. One is to extract and dissolve Ti into Mg melts using different Ti based compounds. Another is to add particles that can act as heterogeneous nucleation sites for $\alpha$-Mg. Jeong et al. [30] claimed that Al$_3$Ti particles were effective as heterogeneous nucleation sites for $\alpha$-Mg in the Mg-3Al and Mg-9Al alloys. In their work, Ti sonotrode was immersed in the melt followed by ultrasonic irradiation to help dissolving the sonotrode material and enhancing the grain refinement. Disregistry model calculations were then performed, which suggested the potency of Al$_3$Ti particles with $\alpha$-Mg. However, it was unclear which factor, the addition of Al$_3$Ti particles or the ultrasonic irradiation, predominated the grain refinement. Furthermore, there were no direct experimental evidences confirming the homogeneous nucleation of $\alpha$-Mg on the titanium aluminide.

Other new grain refiners were also reported. Some were discovered through experimental testing and others through crystallographic calculations. She et al. [31] reported that addition of Sn to AM60 and AM90 alloys led to the formation of Mg$_2$Sn intermetallic. Based on the E2EM model calculations, it was suggested that Mg$_2$Sn particles acted as the heterogeneous nucleation sites for Mg$_{17}$Al$_{12}$ intermetallic, which led to morphology change. The dispersed finer eutectic Mg$_{17}$Al$_{12}$ was
believed to be restricting the grain growth during solidification, and hence, leading to the grain refinement. Another group of researchers [32] claimed that addition of Al-4Nb-1B master alloy to molten AZ91 promoted the formation of NbB$_2$ particles. Thermodynamic calculations showed that NbB$_2$ particles are more favoured to form over Mg- or Al-intermetallic borides. Even though disregistry model calculations confirmed the potency of NbB$_2$ particles with $\alpha$-Mg, the study lacked direct evidences, such as SEM and TEM micrographs, to prove the presence of the nucleants within the Mg grains.

More recently, Liu et al. [33] successfully refined the AZ31 grains with ZnO using suction casting method. Addition of 1.3 wt.% ZnO led to significant grain refinement as well as improvement of the mechanical properties of the alloys. Similarly to previous reports, it was claimed that dissolution of Zn solute and presence of potent ZnO Particles in the melt both led to the grain refinement. The high grain refining efficiency of ZnO in an AZ91 alloys was also reported by Saha et al. [34], who also observed the presence of ZnO particles in the centres of AZ91 grains as shown in the SEM micrographs in Fig. 1. However, further in-depth evidences such as TEM or EBSD might be needed to confirm the nature of the proposed inoculant. As crystal structure of ZnO is extremely similar to that of the $\alpha$-Mg matrix, ZnO particles can potentially act as effective nucleants in the alloys. On the other hand, the cooling curves showed that addition of ZnO led to higher undercooling as a result of the increase in concentration of Zn solute from the reduction of ZnO particles. Hence, ZnO can be regarded as a very promising grain refiner for both non Al-containing and Al-containing Mg alloys.

![Fig. 1: (a) and (b): SEM micrographs for Mg-3.0wt.% ZnO alloy in low and high magnification respectively. (c) EDX analysis for the particle in (b). [34]](image-url)
Chapter 3: Experimental procedures:

3.1 Materials used for casting:

For casting, magnesium ingots were first melted and used as the base material for all cast alloys. After melting, solutes and/or inoculants were added in order to study their effect on the grains of the as-cast alloys. All casting experiments within this PhD were conducted using commercial purity raw materials. In Table 3.1, raw materials used for casting are listed with their addition forms, suppliers and purities to the melt suppliers of all. Detailed casting procedures are listed in section 3.2.

Table 3.1: List of elements/ compounds and their addition forms, suppliers and purity used in casting throughout the PhD

<table>
<thead>
<tr>
<th>Material</th>
<th>Addition Form</th>
<th>Supplier</th>
<th>Purity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Metal ingots</td>
<td>Taiyuan Yiwei Magnesium Industry Co. Ltd. (China)</td>
<td>99.94</td>
</tr>
<tr>
<td>Al</td>
<td></td>
<td>Pacific Aluminium (Australia)</td>
<td>99.96</td>
</tr>
<tr>
<td>Zn</td>
<td></td>
<td>SMC (Australia)</td>
<td>99.995</td>
</tr>
<tr>
<td>Cu</td>
<td></td>
<td>Bohler Uddeholm (Australia)</td>
<td>99.9</td>
</tr>
<tr>
<td>Sn</td>
<td></td>
<td>Alfa Aesar (Australia)</td>
<td>99.9</td>
</tr>
<tr>
<td>Mn</td>
<td></td>
<td>Northern Smelters (Australia)</td>
<td>99.9</td>
</tr>
<tr>
<td>Ca</td>
<td>Mg-9.0wt.%Ca commercial MA</td>
<td>Ganzhou Feiteng Light Alloy Co., Ltd.</td>
<td>99.9</td>
</tr>
<tr>
<td>Zr</td>
<td>Mg-33.0wt.%Zr commercial MA</td>
<td>This MA was made at UQ foundry</td>
<td>N/A</td>
</tr>
<tr>
<td>Si</td>
<td>Al-50.0wt%Si commercial MA</td>
<td>Belmont (USA)</td>
<td>99.0</td>
</tr>
<tr>
<td>Ti</td>
<td>Al-6.0wt.%Ti commercial MA</td>
<td>KBM Affilips (Netherlands)</td>
<td>98.7</td>
</tr>
<tr>
<td>CaO</td>
<td>Ceramic powders (2-5 μm)</td>
<td>Atlantic Equipment Engineers (USA)</td>
<td>99.0</td>
</tr>
</tbody>
</table>

3.2 Casting process:

As a major preparation process for all castings, mild steel crucibles, and all other tools, were coated with boron nitride in order to protect the melt from any foreign impurities. The crucibles and tools were preheated at 200 °C for two hours after the coating. Electric resistance furnace was then used for melting with the temperature set to 740 ±10°C. Batches of 500 to 1000 gm of pure Mg were melted first then potential grain refiners were added. Solutes and/or inoculants were added to molten Mg. Solutes were added to the melt in one of two forms. For solutes with high solubility in Mg and/or with a melting temperature close to that of Mg, such as Al and Zn, metal ingots were directly added to the melt. On the other hand, master alloys were used to add solutes with low solubility in Mg or with much higher melting point than that of Mg such as silicone and titanium.
For inoculants, addition was done in the form of ceramic powders. As it is a bit challenging to directly add powders to the metal melts, ceramic powders inoculants were added in the form of compacted pellets. Powders were first mixed with freshly cut Mg chips then compacted in a die into 20 mm billets with the chip over particle ratio of 4:1 under 50 MPa pressure using a hydraulic press then added to the melt.

After addition, the melt was manually stirred for almost 30 seconds followed by an isothermal hold for 15 to 60 minutes depending on the added solute/inoculant. In order to protect the melt from reacting with the surrounding air, a mixture of 1% SF₆–49% CO₂–50% dry air shielding gas was used. After skimming the dross samples were taken in one of two forms. One, scooping from the melt using a conical steel cup (40 mm in diameter at top, 20 mm in diameter at base and 30 mm high with 1 mm wall thickness) that was preheated by holding on the top of the melt for 30 seconds prior to sampling. The other method was pouring into steel or copper permanent moulds that were preheated at 150 or 200 °C using preheating furnace.

In the next three chapters (Chapter 4, 5 and 6) the main work done throughout the PhD is covered. Even though the scope of all four studies is closely related, there are some differences in the procedures such as the moulds used and compositions of the alloys. Hence, to prevent confusion of the reader, the following paragraphs aim to highlight the major casting procedures in each of the four main studies done in this PhD.

In the first part of Chapter 4, Mg alloys with various addition levels of CaO were prepared. Some Mg-Ca based alloys were also cast for comparison. Samples were then taken using a conical mould. The second part of the chapter focuses on studying the mechanical properties of the as-cast alloys. Hence, two groups of alloys were prepared for comparison, Mg-CaO and Mg-Ca based. Addition levels were kept the same for both base alloys. However, unlike the first part, permanent steel moulds were used to be able to machine tensile samples from the as-cast ingots. More details about the experimental procedures on this study can be found in Chapter 4.

In order to evaluate the solute effect in Chapter 5, various alloys were prepared where the addition levels of the solutes were deliberately selected so that the same Q-values are achieved in different systems. Five eutectic-forming solutes with Mg were chosen for the study. They are Ca, Zn, Al, Ag and Sn. For comparison, two other alloys were cast using the same casting conditions. They are Mg-1.0wt.%Zr and Mg1.4wt.%CaO. After melting, melts were poured in a specially designed V-shaped copper mould preheated at 150°C. By using such a mould, different cooling rates could be achieved at different parts of the ingots. Details about the mould dimensions can be found in chapter 5.

Lastly, a final study has been carried out, reported in Chapter 6, aimed to investigate the effect of solutes addition on the microstructure and hardness of cast Mg-Al based alloys. Various solutes
were added to Mg-3.0wt.%Al and Mg-9.0wt.%Al based alloys. They are Si, Cu, Ca, Sn, Mn and Ti. Cylindrical steel moulds were used for this study. More details on the samples dimensions, compositions and preparation methods are listed in Chapter 6. To summarize, Table 3.2 lists the compositions of all cast alloys prepared throughout this PhD. Also addition levels of solutes/inoculants and moulds used for each experiment are listed.

Table 3.2: Compositions of all cast alloys done throughout this PhD with the moulds used for each experiment.

<table>
<thead>
<tr>
<th>Solutes/ inoculants</th>
<th>Base alloy</th>
<th>Addition level (wt.%)</th>
<th>Mould used</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloys in Chapter 4</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaO</td>
<td>Pure Mg</td>
<td>0.1 0.3 0.7 1 1.5 2 2.5 3</td>
<td>Steel conical mould</td>
</tr>
<tr>
<td>* Mg-1.4CaO, Mg-1Zn-1.4CaO and Mg-1Ca-1.4CaO alloys were prepared for comparison</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>Pure Mg</td>
<td>0.1 0.3 0.7 1 1.5 2 2.5 3</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Pure Mg</td>
<td>1 - - - - - - -</td>
<td></td>
</tr>
<tr>
<td><strong>Alloys in Chapter 5</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>Pure Mg</td>
<td>0.125 0.4 1 - - - - -</td>
<td></td>
</tr>
<tr>
<td>Zn</td>
<td>Pure Mg</td>
<td>0.28 1 2.25 - - - - -</td>
<td></td>
</tr>
<tr>
<td>Al</td>
<td>Pure Mg</td>
<td>0.37 1.2 2.77 - - - - -</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Pure Mg</td>
<td>1 3.25 7.96 - - - - -</td>
<td></td>
</tr>
<tr>
<td><strong>Alloys in Chapter 6</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ca</td>
<td>Mg3Al and Mg9Al</td>
<td>0.5 1 2 3 5 - - - - -</td>
<td>Cylindrical steel mould</td>
</tr>
<tr>
<td>Ti</td>
<td>Mg3Al and Mg9Al</td>
<td>0.02 0.03 0.05 0.1 0.15 - - - -</td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>Mg3Al and Mg9Al</td>
<td>1.5 2 3 5 7 - - - -</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Mg3Al and Mg9Al</td>
<td>0.25 0.5 1 2 3 - - - -</td>
<td></td>
</tr>
<tr>
<td>Sn</td>
<td>Mg3Al and Mg9Al</td>
<td>0.5 1 2 3 5 - - - -</td>
<td></td>
</tr>
<tr>
<td>Mn</td>
<td>Mg3Al and Mg9Al</td>
<td>0.1 0.2 0.5 1 1.5 - - - -</td>
<td></td>
</tr>
</tbody>
</table>

### 3.3 Microstructure characterization:

To investigate the grain size behaviour of the alloys, metallographic specimens were cut from the as-cast ingots, mounted, mechanically polished and then etched for microstructure examination. To reveal the grains, specimens were etched using 100mL, 5g picric acid, 5mL acetic acid and 10mL water etching solution. Polivar polarized optical microscope with a camera was then used to capture images. Captured micrographs were then used to calculate the average grain size using linear intercept technique (ASTM 112-10). Another etching solution was used to reveal the intermetallic phases. After polishing, samples were etched using 2-5% Nital solution and the same optical microscope was used for examination.
For some alloys, studying the nature of the nucleating particle was essential. Hence, in order to find the nucleating particle, selected alloys were further investigated using scanning electron microscopy (SEM). After mechanically polished, samples were examined in a JOEL 6610 SEM. Two SEM modes, i.e. backscattered electron and secondary electron were utilized to find the potential nucleating particle. Using energy dispersive X-ray spectroscopy (EDS), compositions of the potential particles were determined. After spotting the particle, using transmission electron microscope (TEM), further investigations were done in order to crystallographically prove the orientation relationship (OR) between the nucleating particle and Mg matrix. TEM JEOL 2100 was used to obtain spot patterns, bright field and dark field micrographs of the particle and the matrix. TEM foils were prepared in a FEI SCIOS focused ion beam/scanning electron microscope (FIB/SEM) dual beam system. The potential nucleation particle was located with the aid of electron beam. A 1 um thick platinum layer was then deposited on the sample surface covering the area of interest to prevent it from damage caused by the ion bombardment in the following steps. A thin slice of the material perpendicularly to the sample surface was cut by milling two trenches on both sides, with an ion beam current in the range of 3nA-30nA at the acceleration voltage of 30kV. The thin section was then attached to the EazyLift Micromanipulator and cut free from the sample matrix before being glued on to a TEM half-grid. The post thinning process was carried out at much lower ion beam current (0.3nA down to 30pA), followed by final cleaning steps using low voltage polishing at grazing incidence. TEM patterns and micrographs were analysed using Digital Micrograph software.

3.4 Mechanical properties testing:

Hardness testing specimens were cut, ground and polished then Leco LV800 machine was used for Vickers hardness measurement. For tensile, as-cast ingots were machined into standard tensile samples with 20.0±0.4 mm gauge length and 10.0 ± 0.5 mm gauge thickness. All prepared samples were then ground using 600 grit sand papers. The width and thickness of the samples were measured in three locations, with the average being used to calculate the stress. Tests were performed on an INSTRON® testing machine with a crosshead speed of 0.001mm/s and a 5000N load cell. The tensile strain was measured using a pair of extensometers that were attached to the tensile samples. 0.2 proof stress was measured and treated as the yield strength.
Chapter 4: Effects of CaO addition on the grain refinement and mechanical properties of cast Mg alloys

4.1 Chapter overview:

This chapter reports the discovery of CaO as an effective grain refiner for cast Mg alloys. In addition, it also investigates the effect of the new grain refiner on the mechanical properties of as-cast Mg alloys. The outcomes can be regarded as an innovative achievement of this PhD project as the results reported in this chapter are novel.

First, crystallographic matching between CaO particles and α-Mg matrix has been calculated using the E2EM model. The calculation indicated that the FCC-CaO particles can act as nucleants for HCP-Mg. This prediction has been experimentally verified through adding various amount of CaO into Mg melts. Metallographic examination showed the transition of columnar grains to equiaxed grains in the ingots. The columnar-to-equiaxed (CTE) transition was firstly observed at 0.3 wt.% CaO addition. With 0.7 wt.% CaO addition, the average grain size was reduced from ~3330 μm in pure Mg to ~1300 ± 17 μm in Mg-0.7wt.%CaO alloy. During SEM examination, CaO particles were observed at the centres of Mg grains, indicating the possibility that α-Mg nucleated on the CaO particles. Addition of Ca solute to Mg-CaO base alloys led to further grain refinement. However, grain coarsening occurred when adding Al solute. Details on this work are present in Paper 2 entitled with “The influence of CaO addition on grain refinement of cast magnesium alloys”, Scripta Materialia, 2016, vol. 114, page 103-107.

The effect of grain refinement through addition of CaO particles on the mechanical properties of the Mg alloys was investigated and the results were presented in Paper 3. Adding CaO into Mg melt had two possible consequences. One was the reduction of CaO by Mg, leading to the formation of Ca solute in the melt. Another was the survival CaO particles acting as nucleants, promoting the heterogeneous nucleation. Although both consequences could refine the grains, their effect on the mechanical properties was opposite. To clarify their influence on the properties, two groups of samples were prepared. One was Mg-Ca based alloy and another was Mg-CaO based alloy. Microstructure examination showed that, at the same addition level, CaO has higher grain refining efficiency in Mg than Ca solute. Both the grain refinement and solute effect contributed to the improvement of strength of both types of Mg alloys. But, the grain refinement strengthening is more predominated in the Mg-CaO base alloys than that in the Mg-Ca system. Results included in this part of work were published in Magnesium Technology 2017 entitled “Influence of CaO grain refiner addition on the microstructure and mechanical properties of as-cast Mg alloys”, Magnesium Technology 2017, Springer International Publishing, 2017. Page 93-98.
4.2 Associated paper 1:

PAPER 2

The influence of CaO addition on grain refinement of cast magnesium alloys

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The influence of CaO addition on grain refinement of cast magnesium alloys

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Abstract:
CaO was validated as an effective grain refiner for cast Mg alloys. 0.7 wt% CaO addition led to significant reduction in grain size. As CaO particles were reproducibly found within the Mg grains, it was considered that CaO particles promoted heterogeneous nucleation. Additionally, some CaO particles were chemically reduced by Mg, which produced Ca solute and contributed to the grain refinement. The present work indicated that co-existence of active nucleants and solutes with high Q-values in the melt are essential to achieve the highest grain refining efficiency. For Mg alloys, chemical reactions should also be considered at inoculation treatment.

Key words: Grain refinement, Casting, Magnesium alloys, CaO

Aiming at higher mechanical properties, intensive research efforts have been done on Mg alloys. One of the most successful processes to produce both high strength and ductility is grain refinement [1]. Generally, it can be done either before or after solidification. As the latter requires high energy to convert coarse grains into smaller grains at solid state, metal melt treatment is widely used due to its low cost and high efficiency [1]. Specifically, inoculation has been considered as more efficient and reliable technique for melt treatment [2, 3]. The grain refining efficiency of an inoculant is normally dominated by two main factors, i.e., the presence of in-situ heterogeneous nucleation sites and solute elements [1, 4, 5]. A powerful criterion to describe the solute effect is the growth restriction factor, or Q-value [1, 4, 5]. It can be defined as the rate of establishing a constitutionally supercooled (CS) zone ahead of the solid liquid (S/L) interface due to solute segregation. On the other hand, potency of the nucleant can be described as the less energy required activating the nucleation.

In an effective inoculation process, both the solute element(s) with high Q-value and potent nucleants should be available in the melt [1]. The presence of solutes can lead to formation of (CS)
zone ahead of the (S/L) interface where heterogeneous nucleation could be activated according to
the Inter-dependency theory [6]. Therefore, smaller grains can be obtained. The potency of
nucleants depends on two factors. According to the free growth theory [7], nucleation tends to occur
on large particles and for a particular system it can only occur on particles that are over a critical
size. Another is the crystallographic matching between the particle and metal matrix [8, 9]. The
edge-to-edge matching (E2EM) model is not only capable of explaining grain refining behaviours,
but has also been successful in designing new grain refiners [10-12], such as, Al$_2$Ca [13], HfC [14],
AlN [15], Al$_2$Y [16] and ZnO [17] in magnesium alloys.

However, these grain refiners have limitations. For example, the grain refining efficiency of
AlN can only be achieved at higher casting temperature of 760°C and Al$_2$Y only works in Mg
alloys containing over 8wt%Y. Furthermore, none of them are as effective as Zr [18, 19] which is
only valid for non-Al/Mn/Si-containing Mg alloys due to chemical reaction between Zr and these
solutes. Zr master alloys are also expensive and difficult to be added into the Mg alloy melts.
Therefore, in the past couple of decades, considerable efforts have been made to develop new and
more effective grain refiners for cast Mg alloys [1, 4, 20]. The present work reports the grain
refining efficiency of a grain refiner, which was identified from the E2EM calculation, in various
Mg alloys, including pure Mg, Mg1Ca, Mg1Zn and Mg3Al.

Crystallographic calculations based on the E2EM model [21] indicate that the FCC-CaO has
excellent atomic matching with the HCP-Mg matrix. The FCC-CaO has three closed packed planes
{002}_CaO, {022}_CaO and {222}_CaO [22] and two closed packed rows <100>_CaO and <110>_CaO. The
close packed planes and directions associated with the HCP-Mg are [16]: {0002}_Mg, {1120}_Mg, {10-
11}_Mg, <11-20>_Mg, <11-23>_Mg and <1-100>_Mg. By coupling the closed packed planes of both
crystals, pairs of matching planes were identified. Pairs with interplanner mismatch ($f_d$) less than
10%.
Table 1: Misfit and mismatch (>10%) of matching rows and planes calculated using E2EM model between FCC-CaO and HCP-Mg phases

<table>
<thead>
<tr>
<th>Rows</th>
<th>Planes</th>
<th>Possible ORs</th>
</tr>
</thead>
<tbody>
<tr>
<td>f_r</td>
<td>f_d</td>
<td></td>
</tr>
<tr>
<td>Mg CaO 20//110</td>
<td>Mg CaO (0002)//(002)</td>
<td>2.2% Mg//[110]CaO in (0002)Mg//(002)CaO</td>
</tr>
<tr>
<td>Mg CaO 113//110</td>
<td>Mg CaO (101)//(002)</td>
<td>2.26% Mg//[110]CaO in (101)Mg//(002)CaO</td>
</tr>
<tr>
<td>Mg CaO 113//110</td>
<td>Mg CaO (110)//(022)</td>
<td>5.56% Mg//[110]CaO in (101)Mg//(002)CaO</td>
</tr>
</tbody>
</table>

In a similar fashion, pairing of parallel rows found the matching directions with interatomic misfit f_r < 10%. After refining the results, three possible orientation relationships (ORs) could be predicted which implies a high potential for CaO to be an effective nucleant for Mg. Calculated f_d, f_r, and possible ORs are listed in Table 1.

It is worth mentioning that the above prediction of the CaO potency has been, to some extent, supported by preliminary results from other researchers [23, 24]. But, CaO has not deliberately inoculated as a nucleant for Mg alloys. Discussions on the mechanism have been restricted to the presence of other compounds in the melt, such as Al2Ca and Mg2Ca [23, 24]. However, a number of issues still remain unclear. For example, whether CaO itself can promote heterogeneous nucleation?

From the above crystallographic calculations, it is reasonable to conclude that CaO particle can possibly act as a potent nucleant for α-Mg grains. In addition, reduction of CaO in Mg melt has been confirmed [25]. Hence, it is expected that the presence of high Q-value Ca solute, in Mg melt (Q_{Ca}=11.94 K [4]), may also contribute to the reduction in grain size. Therefore, CaO meets all the essential criteria for an effective grain refiner for cast Mg alloys.

Commercial purity Mg, Zn, Al ingots and Mg-9wt%Ca master alloy were used to prepare the alloys in an electrical resistance furnace using boron nitride coated mild steel crucibles. The set temperature for melting was 730°C. The melts were protected by a mixture of 1% SF6–49%CO2–50%air cover gas. CaO powder with particle size of 2-5 μm was mixed with Mg chips (ratio 1:4). Then they were compacted into 20 mm in diameter billets with height of ~10 mm. After adding the billets, the melt was manually stirred then isothermally held for 15 minutes. Samples were taken using a pre-heated mild steel conical cup. The dimensions of the cup were 40 mm in diameter at top, 20 mm in diameter at base and 30 mm high with 1 mm wall thickness.
Samples were cut, mounted, polished then etched. Polarized light optical microscope was used to examine the grains. Using the lineal intercept method [26] grain sizes were calculated. The average of the measured values was used as the mean grain size of the cast alloys. Microstructure of the alloys was examined in a JEOL6610 SEM and EDX analyses were performed to estimate the chemical compositions of phases in the alloys. Samples were also examined in a JEOL 2001 transmission electron microscopy (TEM). A FEI Dual FIB/SEM-SCIOS focused ion beam (FIB) milling system was used to prepare the TEM foils so that CaO particles at the centre of Mg grains can be identified.

Addition of CaO particles to pure Mg melt effectively changed the morphology of grains from columnar to equiaxed. The columnar-to-equiaxed (CTE) transition was firstly observed at addition of 0.3wt%CaO. Figs.1 (a) to (d) show typical optical micrographs of the as-cast pure Mg with various addition levels of CaO. The variation of measured average grain size with CaO addition level is plotted in Fig.1 (e). It can be seen that the grain size was dramatically reduced from ~3330 to ~1300 ±17 μm after 0.7wt%CaO was added, but further addition of CaO only resulted in marginal refinement.

As mentioned above, a recent study [25] confirmed that the added CaO in molten Mg can be chemically reduced to Ca and MgO even though the standard free energy of formation of MgO is higher than that of CaO [27]. The reduced Ca may contribute to the grain refining as a solute. To clarify this possibility, two different Mg melts were prepared. One was Mg-1.0wt%Ca binary alloy. The other was prepared through direct addition of 1.4wt%CaO into pure Mg melt. If all the 1.4wt% added CaO was chemically reduced, the same amount (1.0wt%) of Ca solute would be brought into the Mg melt [23, 25, 28]. After casting, the optical micrographs of both alloys are shown in Figs.2 (a) and (b). The grain size of the Mg-1wt%Ca alloy is ~1700 μm and it is ~1200 μm for the Mg-1.4wt%CaO alloy. As the two alloys were produced using the same pure Mg ingot as raw materials, the accompanied residual impurities or inclusions, which may affect the nucleation and growth, were the same in both alloys. Thus, the finer grains in the Mg-1.4wt%CaO alloy are highly likely attributed to heterogeneous nucleation. The possible nucleants are the chemical reduction product MgO and the remaining CaO particles that were not completely reduced. According to the E2EM model calculations, MgO is not considered as a good nucleant due to the large lattice mismatch with Mg. Previous investigations on the grain refining efficiency of MgO in Mg alloys showed that the inoculation effect of MgO only occurred at enhanced casting condition through intensive melt shearing [29, 30]. Kim and co-workers [15] found a significant grain reduction of an AZ91 alloy after addition of 0.6wt%MnCO₃ and considered that MgO, Al₄C₃ and Al₆Mn₅, which were possible products from decomposition of the MnCO₃ in the Mg melt, served as the heterogeneous nucleation sites. But, no clear evidence was provided showing the nucleation of α-Mg occurred on which type
of the particles. Because Al₄C₃ is commonly accepted as an effective nucleant for α-Mg, highly likely the grain refining was resulting from this inoculant in Kim’s work. Hence, at present, CaO particles can be regarded as the heterogeneous nucleation sites.

Fig.1: (a-d) Typical metallographs for as-cast Mg alloys with different CaO additions, (a) no addition, (b) 0.3, (c) 0.7 and (d) 1.0wt%CaO. (e) Relationship between grains size and wt% of added CaO.

Fig.2: (a), (b) and (c), Typical metallographs for as-cast Mg alloys with (a) 1.0wt%Ca, (b) 1.4wt%CaO, (c) 1.0wt%Ca+1.4CaO. (d) SEM back scattered micrograph for as cast Mg-3wt%CaO sample.

To verify this hypothesis, the microstructure of the Mg-CaO alloy was further examined in SEM together with EDX analysis. A typical back scattered electron micrograph of the as-cast alloy is presented in Fig.2 (d). The possible nucleation particles, named A and B, can be clearly seen within the grain in addition to the eutectic structure typically observed along the grain boundaries in Ca-containing Mg alloys [31]. Referring to the EDX results, the particles A and B are possibly CaO due to the higher concentration in Ca and O elements compared with those of the matrix (point C). Because the particle size is around 1 μm, which was much smaller than the size of the electron probe for EDX analysis, the CaO cannot be fully verified based on only the EDX results of these two particles. Thus, the microstructure was further examined in TEM.
Foils were prepared using focused ion beam (FIB) milling method. CaO particles at the centre of Mg grains were picked up together with their surrounding matrix then milled. Figs.3 (a) and (b) show the typical bright field TEM micrographs of the nucleus in Mg matrix. After tiling the TEM sample to the [01-10]$_{Mg}$ zone axis the diffraction pattern obtained from the particle is shown in Fig.3 (c). Indexing the diffraction pattern confirmed the particle as CaO. However, the homocentric diffraction rings characterize the nanometre or submicron scaled structure. This implies that the identified CaO ‘particle’ in both optical microscopy and SEM is actually nanostructured CaO. This might be resulted from the manufacturing process of the CaO powder. The interface between the nanostructured CaO particle and the Mg matrix can be further examined at high magnification as shown in Fig.3 (b). Due to the nanostructure of the particle, no reproducible crystallographic orientation relationship could be determined between the CaO particles and their surrounding Mg matrix. However, the integration of the CaO particle and the matrix as shown in Fig.3 (b) suggests that CaO is a very promising grain refiner for cast Mg alloys. Based on the free growth model [7], the nucleating potency of the small particles should be lower than that of the big particles as activating small nucleation particles requires higher undercooling than that of the big particles. Hence, it is expected that micrometre sized CaO particles should be more potent than the nanostructured ones. Continuing research on grain refinement of adding CaO particles of which each particle is a single crystal is currently being undertaken.

It was noted that, most recent researches have focused either on the inoculation or on the solutes effect. The conventional combined effects of heterogeneous nucleation and solute effects on grain refinement were less mentioned. In order to re-emphasize the importance of the combined effect and to further test the efficiency of CaO as a nucleant in cast Mg alloys, 1.4wt%CaO was added into three Mg binary alloys containing solutes with high Q-values. They were Mg-1.0wt%Ca, Mg-1.0wt%Zn and Mg-1.0wt%Al. As shown in Fig.2 (c), addition of 1.4wt%CaO inoculant in to the Mg-1.0wt%Ca alloy led to further grain refinement. The grain size has been reduced to ~ 620 μm, which is smaller than that of both the Mg-1.0wt%Ca (~ 1700 μm) and the Mg-1.4wt%CaO (~ 1200 μm) alloys. Similarly, as shown in Figs.4(a) and (b), addition of 1.4wt%CaO into the Mg-1wt%Zn alloy also led to about 56% further reduction in grain size compared with the binary alloy (measured grain size of Mg-1wt%Zn alloy was ~1042.6 μm). The obtained mean grain size of the Mg-1wt%Zn-1.4wt%CaO alloy was ~ 470 μm, which is smaller than that of the Mg-1.4wt%CaO alloy in Fig.2 (b). Obviously, such further grain refinement was attributed to the addition of CaO.

The effect of CaO particles addition on grain refinement of the as-cast Mg-Ca and Mg-Zn binary alloys can be well understood in terms of the interdependency theory [6]. After addition, the fraction of CaO particles which had not been chemically reduced in the Mg melt not only promoted heterogeneous nucleation at beginning of the solidification, but also restricted the grain growth
through continuing nucleation within the constitutional supercooling (CS) zone at front of the solid/liquid interface. As the formation of CS zone relies on the solute segregation at the front of the solid/liquid interface, in the Mg-1.4wt%CaO system, only the small amount of Ca produced from the chemical reduction contributed to the formation of the CS zone. Thus, further thermal undercooling was required to activate the heterogeneous nucleation on the CaO particles within the CS zone. Hence, its grain refining efficiency was relatively low. After adding CaO into the Mg-Ca and Mg-Zn binary alloys, solutes Ca and Zn with high Q-values, significantly contributed to the formation of the CS zone. As a result, heterogeneous nucleation on CaO particles was accelerated within the CS zone. This effectively restricted the grain growth, resulting in further grain refinement.

Fig.3: (a) Bright field image for CaO particle in Mg matrix. (b) Higher magnification for matrix/particle interface. (c) Spot pattern of CaO particle after tilting along [01-10]Mg zone axis.

Fig.4: Typical micrographs for as cast (a) Mg-1wt%Zn, (b) Mg-1wt%Zn+1.4wt%CaO, (c) Mg-1wt%A1 and (d) Mg-1wt%A1+1.4wt%CaO

However, addition of 1.4wt%CaO into the Mg-1.0wt%A1 binary alloy led to grain coarsening as shown in Figs.4 (c) and (d). The grains of the Mg-1.0wt%A1-1.4wt%CaO alloy are not only coarser than the Mg-1.0wt%A1 alloy, but also coarser than the Mg-1.4wt%CaO alloy. It is considered that such coarsening is related to chemical reactions occurred in the Mg melt. According to thermodynamic calculations, the free energy difference $\Delta G = -167.25$ kJ/mole for the reaction $\text{Mg} + 2\text{Al} + \text{CaO} \rightarrow \text{Al}_2\text{Ca} + \text{MgO}$ at 727°C [32]. Hence, after CaO was added into the molten Mg-1.0wt%A1 alloy, the reaction consumed the majority of Al solute in the alloy. As a result of the
reduction in Al content in the melt, solute effect on grain refinement was weakened, even eliminated. Although the produced Al$_2$Ca can act as a nucleant for $\alpha$-Mg according to Jiang et al. [13], who experimentally and theoretically verified that Al$_2$Ca can promote the heterogeneous nucleation of Mg, the grain refining efficiency is limited due to the lack of solute in the present work. But, Al$_2$Ca, together with the remaining CaO may be responsible for the formation of equiaxed grains as shown in Fig.4 (d).

In the past a few decades, a number of theories/models have been developed to understand the mechanisms of grain refinement in cast metals [1, 4, 33]. But, none of them can fully explain all the phenomena associated with grain refinement in cast metals. The present results suggest that effective grain refinement can only be achieved with the presence of enough amount of solute with high Q-value along with effective nucleant in the melt. This effective nucleant can be externally added or in situ formed. But, it must be thermally and chemically stable. Otherwise, its effect in promoting heterogeneous nucleation would be weakened, even eliminated. For instance, ZnO is an effective nucleant for $\alpha$-Mg from crystallographic point view [17], but its grain refining efficiency is very limited because ZnO can be rapidly chemically reduced by Mg in the melt [17]. In addition, as Mg has very high chemical reactivity, particularly at elevated temperatures, the externally added nucleants may chemically react with Mg, leading to unexpected decrease in grain refining efficiency. This probably takes partial responsibility for the difficulty in developing new and more effective grain refiners for Mg alloys, Mg-Al based alloy in particular.

(1). Addition of CaO led to effective grain refinement in pure Mg and in some Mg alloys, such as the Mg-1.0wt%Zn alloy. The solute effect of Ca produced from the chemical reduction reaction of CaO by Mg and the remaining CaO as nucleant cooperatively contributed to the grain refinement.

(2). The highest grain refining efficiency in cast metals can be achieved when fulfilling the presence of both, a) enough amount of high Q-value solute and b) thermally and chemically stable effective nucleants in the melt.

(3). Due to the high chemical activity, the chemical reaction before solidification must be taken into account when developing new and more effective grain refiners for cast Mg alloys, Mg-Al based alloys in particular.

References:


2935-2949.
4.3 Associated paper 2:

PAPER 3

Influence of CaO grain refiner addition on the microstructure and mechanical properties of as-cast Mg alloys

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Influence of CaO grain refiner addition on the microstructure and mechanical properties of as-cast Mg alloys

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Abstract:

The current work compares the effects of Ca solute addition with CaO powder addition on the grain refinement and mechanical properties of cast Mg alloys. Two groups of samples were prepared. One was through directly adding Ca solute into the Mg melt using Mg-Ca master alloy and another was through the addition of CaO powder. Although as-cast grain size of both alloys was very close, the Vickers hardness values of Mg-Ca alloys were higher than that of Mg-CaO alloys. Based on the tensile test results, empirical relations between elastic modulus, ultimate tensile strength, yield strength and elongation vs alloys concentrations were established. It has been found that grain refinement is not the predominated strengthening mechanism in both alloys, but the effect of grain refinement strengthening is higher in the Mg-CaO alloys than that in the Mg-Ca alloys.

Keywords: Casting, Mg alloys, Mechanical properties, CaO, Grain refinement

1. Introduction:

Recently, the interest of automotive and aerospace industries in magnesium (Mg) and its alloys have been increasing rapidly due to its high specific strength and abundance. However, Mg hexagonal-close-packed (HCP) crystal structure has limited slip systems with the majority of slip taking place on crystal’s basal place. This makes the metal inherently susceptible to low ductility and brittle fracture, and thus, limits its applications. Hence, in the last couple of decades, extensive research efforts have been made to improve the mechanical properties of Mg alloys. One very promising technique found is grain refinement by inoculation due to its low cost, reproducible successful results and ease in application [1, 2]. Grain refinement not only can simultaneously improve the yield strength, ductility and toughness of the alloys, but also eliminates the formation of columnar structure which increases the quality of wrought alloys [3]. Recently, CaO was
reported as an effective grain refiner for cast Mg alloys [4]. Decomposition of added CaO powder introduced Ca solute in the melt, which was believed to restrict the grain growth whilst undissolved powder particles acted as heterogeneous nucleation sites for new grains. However, it is remaining unclear to what extent this grain refinement affect the mechanical properties. In addition, as the grain refinement of the added ceramic CaO particles in the melt was subject to reduction to Ca, it would be interesting to know the contributions of both the grain refinement and non-grain refinement, such as the Ca solid solution strengthening and the effect of the CaO particle, to the strength of the alloys.

Many strengthening mechanisms have been extensively studied in various Mg alloys [5-9]. Strengthening can be achieved using one or more approaches, such as solid solution strengthening [10, 11], grain refinement [12], precipitation [9] or strain hardening [13, 14]. Unfortunately, due to the nature of CaO behaviour in Mg alloys, both grain refinement and none grain refinement strengthening affect mechanical properties due to the presence of Ca solute. Thus, the current work aims to compare the mechanical properties of the Mg-Ca alloys with the Mg-CaO alloys in order to distinguish the contribution of grain refinement strengthening from other strengthening mechanisms.

2. Experimental procedures:

2.1. Casting:

Casting process was performed using commercial purity Mg ingots. First, pure Mg was melted in boron nitride coated mild steel crucibles. Temperature was set to 730 ± 5 °C in an electrical resistance furnace. A mixture of 1% SF6–49% CO2–50% dry air cover gas was used to protect the melts from oxidation. Grain refiners (Ca or CaO) were then added to the melt and the addition levels were 0.1, 0.3, 0.7, 1 and 1.5wt. % for both Mg-Ca and Mg-CaO alloys. Mg-9wt.%Ca master alloy was used for the addition of Ca solute in the Mg-Ca binary alloy preparation. To add CaO particles into the Mg melt, CaO powder with particle size 2-5 μm was firstly mixed with Mg chips (ratio 1:4), and then they were compacted into 20 mm in diameter billets with height of ~10 mm. These billets were then directly added into the Mg melt. After adding the grain refiners, the melt was manually stirred then isothermally held for 15 minutes before casting. Two different moulds were used. One was for tensile test samples with a the ingot size of 156 mm long, 39.5 mm wide and 180 mm high. Another was for hardness test and microstructure examination. It was of a cylindrical shape with ingot size of 200 mm height and 20.5 mm in diameter.

2.2. Tensile Test

Tensile test specimens were machined from the cast ingots. Fig.1 shows a schematic
drawing of the tensile test samples. Dimensions labelled in Fig.1 are as follows: \( L_0 = 20.0 \pm 0.4 \) mm, \( L_c = 25.4 \pm 1 \) mm, \( L_t = 52.0 \pm 1 \) mm, \( b = 4.2 \pm 0.2 \) mm, \( a = 3.0 \pm 0.2 \) mm, transition radius = \( R = 4.2 \) mm minimum gripped end with= 10.0 ± 0.5 mm.

Fig. 1: schematic drawing for tensile test sample used in the current work.

Prior to testing, 600 grit SiC sand papers were used to grind the sample surface. 4 samples were tested for each composition. The width and thickness of the samples were measured in three locations, with the average being used to calculate the stress. The testing was performed on an INSTRON® test machine with a crosshead speed of 0.001 mm/s and a 5000N load cell. The tensile strain was measured using a pair of extensometers that were attached to the tensile samples. 0.2 proof stress was measured and treated as the yield strength.

2.3. Hardness

Prior to testing, samples were cut and polished. Then the hardness was measured on a Leco LV800 AT Vickers hardness tester. The test was performed through applying 5 kg load for 10 seconds. On each sample 10 measurements were conducted to ensure the veracity of the result.

2.4. Microstructural Characterization

20.5 mm in diameter and 10 mm thick samples were directly cut from the as-cast ingots. After mechanical grinding and polishing the samples were etched using different etchants depending on the purposes. 2% Nital solution was used for microstructure analysis and an etching solution consisting of 2.5 g picric acid, 50 ml ethanol, 2.5 ml acetic acid and 5 ml distilled water was used for grain size examination. All samples were examined in an optical microscope with polarized light. Average grain sizes were measured using the linear intercept method (ASTM E112-10). A total of 3 images were used to calculate the grain size for each composition. The images were taken in different regions of the casting, at the centre, the edge and in between of the centre.
and edge of the ingot. JEOL-7001F SEM with EDS was used for SEM imaging and analysis.

3. Results and discussion:

3.1. Alloy concentration vs Grain size.

Fig. 2 shows typical optical micrographs of the as-cast Mg alloys with various additions of Ca and CaO. It can be noted that 0.1 and 0.3 wt.% (Ca or CaO) additions could not get rid of the columnar structures and the columnar to-equiaxed (CTE) transition was firstly observed at addition of 0.7wt.% in both alloys. This addition level for CTE is different from that reported in reference [4], which reported the addition of 0.3wt.% CaO led to the disappearance of the columnar structure. Such difference is probably attributed to the different casting conditions. Further addition of Ca solute or CaO particles led to further decrease in the mean grain size in both alloys.

![Fig. 2: Typical optical micrographs for as-cast (a-e) Mg-CaO and (f-j) Mg-Ca binary alloys at various addition levels. (a and f) 0.3 wt.% , (b and g) 0.7wt.%, (c and h) 1.0wt.% and (d and i) 1.5wt.%.

The measured mean grain size was plotted against the amount (in wt.%) of Ca/CaO added in Fig.3. Both CaO and Ca containing alloys shared a similar trend. At low addition levels (0.1 and 0.3 wt.%), slight increase in the grain size was achieved due to the presence of columnar grains structure. Then, noticeable grain refining was observed at 0.7 wt.% addition of Ca solute as grain size reduced from ~520.6 μm to ~278.5 μm. Further increasing the Ca addition level to 1.0wt.% only led to a slight reduction of the grain size to ~190.2 μm. However, with increasing in addition level from 0.7 wt.% CaO to 1.0 wt.% CaO, the average grain size was remarkably reduced from ~408 μm to ~150.2 μm, which is ~71% smaller than that of pure Mg. When the addition level was over 1.5 wt.%, the reduction in grain size was very marginal which come in consistence with the results reported in [14].
Fig. 3: Relationships between grain size and wt.% of added Ca and CaO.

It is important to clarify that the amount of Ca solute is always less in CaO containing alloys if the same grain refiner level was added in two alloys. For instance at 1wt.% addition level, 100% decomposition of 1.0 wt.% CaO particles will only lead to ~ 0.7wt.% Ca solute presence in the melt. On the other hand, ~1.0wt.% Ca solute will be introduced in Mg-1.0wt.%Ca alloy. Even though, the amount of Ca solute in the Mg-CaO samples is less than that in the Mg-Ca alloys, grain size values were close in both alloys which highly likely due to the role played by CaO nucleants in the grain refinement of the Mg-CaO alloys.

3.2 Alloy concentration vs Hardness:

The variation of the micro-hardness of all alloys with the additive level was plotted and presented in Fig.4. The effect of 0.1 and 0.3wt.% additions was very marginal in both systems. This is consistent with the microstructure showing in Fig 2 (a, b, f and g), where no difference in the columnar structure was observed. At such small addition levels, it is considered that all the added Ca or reduced Ca from the CaO was dissolved into Mg with ignorable solid solution hardening effect.
Figs. 5 (a and b) show the single phase microstructure in the Mg-0.3wt.%Ca and Mg-0.3wt.%CaO alloys. No any intermetallic compound particles can be observed, such as the Mg$_2$Ca, which was believed act as a hardening phase in Mg alloys [15]. As shown in Fig. 4, when the addition level is over 0.7wt.%, the hardness increased linearly with the concentration of Ca or CaO. But, the Mg-Ca alloys showed higher hardness than with the Mg-CaO system. Since the grain sizes of both alloys were very close (Fig. 3), the higher hardness of Mg-Ca alloys can be attributed to the high content of Ca, which resulted in the formation of Mg$_2$Ca, as shown in Fig. 5 (c and d). To further clarify the nature of the secondary phase, samples were analysed under the SEM. As shown in Fig.6, EDS analysis suggest that the visible black precipitates, which are believed to be the secondary phase, in Fig. 5 (c and d) are Mg$_2$Ca intermetallic compounds which further supports the claim that Mg$_2$Ca is the major contributor in higher hardness values obtained in Mg-Ca alloys.
3.3. Alloy Concentration vs tensile properties

Fig. 7 shows the relationships between addition levels and tensile properties. From the graphs, addition of Ca or CaO seems to have no effect on the elastic modulus as shown in Fig.7 (a). Based on the literature, the current results were expected. Work by Caceres et al. [16] showed that there was only a minor increase in modulus with increasing Ca solute for AZ series, which peaked at 2.0 at.% and then decreased again. Similarly, in Fig.7 (b) ultimate tensile strength showed almost no change with Ca and CaO various addition levels. This no change in elastic modulus and UTS with increasing the addition level of Ca or CaO might be the result of two different effects. While grain refinement strengthening improves both yield strength and elongation, the brittle nature of Mg$_2$Ca intermetallics, as a result of Ca solute presence in the melt, can negatively affect the ductility. Interference of both effects with each other can lead to obtaining the current results.

On the other hand, graphs in Fig.7 (c) show an increase in the yield strength, which is represented as 0.2 offset stress, with increasing addition levels in both alloys groups. It can be noted that the trend and values of both systems are very close which strongly suggests that both Ca and CaO have the same effect on the yield strength when added to Mg at the same levels. Conversely, elongation of the alloys was found following a downtrend with increasing addition levels of grain refiners as shown in in Fig.7 (d). However, Mg-Ca based alloys showed less elongation than Mg-CaO alloys at the same addition levels. From the results it is clear that addition of both Ca solute and CaO powder led to strengthening of the alloys which affected the mechanical properties. But, the remaining question here is still, which system has higher grain refinement strengthening than the other?
Fig. 7: Relationships for Ca and CaO containing Mg alloys between addition level and (a) elastic modulus, (b) ultimate tensile strength, (c) yield stress and (d) elongation.

One way to answer this question is through plotting, the well-established relationship for mechanical properties, the invers proportionality between yield strength and elongation. Fig. 8 shows the regression of all tested alloys and it can be seen from the slopes that CaO containing samples showed less ductility scarification with yield strength which suggests that grain refinement strengthening component in CaO containing samples is higher than that in Ca containing ones. On the contrary, Ca containing samples indicate more solution strengthened or precipitation strengthened effects where the yield strength is increased with significantly sacrificing ductility.

Fig. 8: Relationship between strain at break and yield stress of Ca and CaO containing Mg alloys.
4. Conclusions:
- Effects of direct addition of Ca solute or CaO powder led to smaller grains in Mg alloys. The grain refining efficiency was very close with both additions.
- Presence of higher number density of Mg$_2$Ca intermetallics in Mg-Ca alloys led to obtaining higher hardness values than Mg-CaO alloys.
- Grain refinement strengthening effect interfered with Mg$_2$Ca brittle nature resulting in no change in elastic modulus and ultimate tensile strength for both systems.
- Yield strength increased with increasing the addition level of both Ca and CaO whilst elongation was reduced.
- In both systems, grain refinement was not the only strengthening mechanism but CaO was found to increase the grain refinement strengthening component than Ca solute.

5. References:


Chapter 5: Combined effect of cooling rate and grain refiner on as-cast magnesium grains.

5.1 Chapter overview

In addition to the inoculation treatment, solidification cooling rate is another major factor that controls the microstructure of cast metals. Generally, higher cooling rate leads to finer grains. In order to understand the effects of solidification cooling rate on the final grain size of as-cast Mg alloys, we have designed a V-shaped copper mould that produces various cooling rate along the height of the mould. A number of Mg alloys were cast in this V-shaped mould. Higher cooling led to finer grains in most alloys, including pure Mg. However, in some alloys that contained effective refiners, such as Zr, CaO and Al, grain coarsening was observed at the highest cooling rate at the tip of the mould. The result can be well-understood in terms of the interdependence theory. More details of this work were reported in Paper 4, which was published recently under the title “Grain coarsening of cast magnesium alloys at high cooling rate – a new observation”; in Metallurgical and materials transactions A 48 (1) (2017): 474-481.
5.2 Associated paper:

PAPER 4

Grain coarsening of cast magnesium alloys at high cooling rate – a new observation

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Grain coarsening of cast magnesium alloys at high cooling rate – a new observation

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Key words: Grain refinement, Casting, Magnesium alloys, Grain coarsening

Abstract

Most studies in the area of grain refinement have always taken for granted that higher cooling rate results in finer grains. However, when microstructural variation of the as-cast Mg with cooling rate was investigated using a specially designed V-shape copper mould, the results were different. Although fast cooling during solidification led to microstructural refining in pure Mg, grain coarsening was observed at a higher cooling rate in Mg alloys that were inoculation treated with 1.0wt%Zr and 1.4wt%CaO, and in the Mg-Al binary alloys. It is considered that the grain coarsening at higher cooling rate was attributed to the smaller constitutional undercooling zone formed at fast cooling due to the high temperature gradient in the three Mg alloys. These results can help in redefining the role of cooling rate in the grain refinement process.

1. Introduction:

Grain refinement of cast metals has been widely accepted as an effective approach to produce alloys with improved mechanical properties, good castability and better formability \cite{1, 2}. Generally, grain refinement of cast metals can be achieved through stirring during solidification, such as magnetic stirring \cite{3-5} and supersonic stirring \cite{6-8}, melt treatment by inoculation \cite{2, 9, 10} and fast cooling \cite{11-13}. Inoculation treatment is more practical and widely used in industry due to its low cost and high reproducibility. The process is generally associated with addition of solutes, which is believed to restrict the grain growth, and adding nucleants that promote heterogeneous nucleation. The grain growth restriction effect of solutes can be described by the growth restriction factor, which is quantified as Q-value \cite{14-15}. In binary systems, the Q-value is calculated by linking the liquids gradient (m) with the alloy composition (C\textsubscript{0}) and the partitioning coefficient (K) using the equation, \[ Q = m C\textsubscript{0} (K - 1). \]
This value represents the capacity of the solute to create a constitutional undercooling zone at the front of the solid/liquid (S/L) interface as a result of the solute segregation, which facilitates the heterogeneous nucleation [16]. The effective nucleant refers to solid particles in the melt that are crystallographically, chemically and thermodynamically compatible with the primary solid to be formed [17, 18] and are big enough [19] to promote heterogeneous nucleation. The nucleants can be either in-situ formed, such as the Al$_3$Ti particles for refining the Al alloys through subsequent addition of the Al-5Ti-1B master alloy and the Al$_2$Y particles formed in the Mg-Y system after adding Al [20], or externally added to the melt as foreign particles, such as the Zr particles [21], the ZnO and the CaO [22, 23] for refining the non-Al-containing Mg alloys. In most cases, the highest grain refining efficiency can be achieved when both solutes with high Q-values and effective nucleants co-exist in the melt [2, 22, 23]. The high grain refining efficiency of Zr particles for non-Al/Si/Mn-containing Mg alloys is attributed to both the very high Q-value of Zr in Mg melt and the Zr particles that are effective nucleants [2, 21, 24, 25]. Recent work [22] also indicated that CaO can effectively refine the pure Mg because CaO particle itself can be an effective nucleant and Ca, which formed through partial reduction of the CaO by Mg, is associated with high Q-value in the Mg melt.

Another parameter that highly affects the final grain size is cooling rate [26]. It is commonly accepted that fast cooling leads to grain refinement in metal casting because of the large thermal undercooling that facilitates the nucleation [11, 12, 27-30]. In addition, considerable studies also verified that the temperature gradient from the mould wall to the centre of the melt also significantly affects the as-cast microstructural morphology [13, 31, 32] because the temperature gradient defines the size of the constitutional undercooling zone. In alloys, the constitutional undercooling may lead to growth instability of the solid phase, promoting dendrite formation, which causes grain coarsening. However, if there are sufficient effective nucleants in the liquid, additional heterogeneous nucleation would occur within the constitutional undercooling zone, which inhibits the growth of the existing grains and therefore leads to grain refinement [2, 9, 22, 33]. In addition, recently, Fan and co-workers’ work [34] demonstrated that, at enhanced cooling condition, such as high pressure die casting, the grain refining efficiency of Zr is not as good as MgO, even though Zr has been considered as a much better nucleant than MgO due to the crystal structure similarity between Zr and Mg. Thus, it looks like higher cooling rate does not always lead to grain refinement. Hence, the present work aims to study and understand the combined effects of cooling rate and inoculation treatment on the as-cast grain size of Mg alloys. The outcome may help to understand the grain refinement mechanism by inoculation and to provide theoretical guidance in developing more effective inoculation treatment methods and then further refine the grains of cast Mg alloys.
2. Experimental:

In the present work, seven alloy melts were prepared in an electrical resistance furnace using boron nitride coated mild steel crucibles. They are pure Mg, Mg-1.0wt%Zr, Mg-1.4wt%CaO, Mg-1.16wt%Al, Mg-2.8wt%Al, Mg-0.94wt%Zn and Mg-2.26wt%Zn. Addition of 1.0wt%Zr and 1.4wt%CaO was based on previous work [22, 24, 25], in which the most significant grain refinement was achieved. The set temperature for melting was 730°C. The melts were protected by a mixture of 1% SF$_6$–49%CO$_2$–50% dry air cover gas. Commercial purity Mg ingots were used to make the alloys. Zr was added using a Mg33.0wt%Zr master alloy. A mixture of CaO powder with particle size of 2–5 µm and Mg chips was compacted into small billets (20 mm in diameter and ~10 mm in height), which were then used to add CaO into the melt. Metal chips were used for the addition of both Al and Zn. After adding the inoculants, the melts were manually stirred for 30 seconds followed by isothermal holding for 15 minutes prior to pouring.

In order to achieve different cooling rates along the samples, a V-shaped mould made of pure copper was made and used for casting of the Mg alloys. The cross section of the mould is shown in Fig. 1 (a). All casting equipment, including the mould, were coated with boron nitride and preheated at 150°C. Three K-type thermocouples were placed at three different positions in the mould before pouring the melt to measure the cooling rates. The measured average cooling rates at the same positions in the mould were almost the same for all the alloys. In addition, the Mg cooling rate in the V-shape mould was also simulated using a commercial software package MATLAB [35]. The results are shown in Fig. 1 (b).

Samples were mounted then ground using silicon carbide papers before polishing. Using 100 mL ethanol, 5 g picric acid, 5 mL acetic acid and 10 mL water, samples were etched for 5 seconds then examined in an optical microscope using a polarized light. Grain size was measured using the linear intercept method [36].

3. Results and discussion:

The orange dots in Fig. 1 (a) indicate the thermocouple positions in the copper V-shape mould for measurement of cooling rate during solidification. Results showed different cooling rates along the ingot. They were $14.8 \pm 5.4^\circ$C/sec at position A, $6.7 \pm 2.7^\circ$C/sec at position B and $3.8 \pm 1.2^\circ$C/sec at position C. in Fig. 1 The simulated cooling rates in the virtual V-shape mould are shown in Fig. 1 (b). The cooling rates at the corresponding positions to the real mould were $18.5^\circ$C/sec at position A, $7.6^\circ$C/sec at position B and $0.38 – 4.02^\circ$C/sec around position C, which agree very well with the experimentally measured cooling rates. This verified the correctness of the simulation. Hence, it is reasonable to consider the variation of cooling rate of Mg alloys in the
copper V-shape mould varies from 0.38°C/sec to 36.79°C/sec. After casting, metallographic samples were cut from different positions in the ingots as shown by the shadowed areas in Fig. 1 (a).

![Diagram](image)

Fig. 1 (a) Schematic drawing showing the cross section of the V-shape mould and the positions, where the cooling rates were experimentally measured using thermocouples; (b) the simulation of the cooling rates along the longitudinal direction on the cross section of the virtual V-shape mould.

Fig. 2 shows typical micrographs taken from the different positions on the pure Mg ingot. Positions A, B and C in Fig. 2 correspond to the same positions in Fig. 1. In Fig. 2, columnar structure is observed throughout the ingot (position B and C) even though the columnar structure was refined at higher cooling rate near the tip of the V-shape mould (position A). This result was expected. In pure Mg melt both the effective nucleants and solutes are very limited. Thus, direct nucleation in the melt was difficult. Due to the fast cooling associated with the cooper mould, nucleation occurred on the mould wall. Nuclei with preferred orientation rapidly grew into the melt in the opposite direction to the heat flow, forming the columnar structure. At the tip of the mould, the high cooling rate enabled nucleation to occur at large undercooling, which increased the nucleation rate on the mould wall. Thus, finer columnar structure was produced.

![Micrographs](image)

Fig. 2 Typical polarized light microscopy micrographs of as-cast pure Mg at different positions in the ingot cast in the V-shape cooper mould.
Addition of grain refiners (inoculants and/or solutes) was found being very effective in eliminating the columnar structure and refining the equiaxed grains as shown in Figs. 3 and 4. Fig. 3 shows typical optical micrographs of Mg-1.0wt%Zr and Mg-1.4wt%CaO. Away from the mould tip (positions A2, B and C), where the cooling rates were roughly below 30°C/sec, higher cooling rate led to finer grains.

![Fig. 3 Typical polarized light microscopy micrographs of the as-cast Mg-1.0wt%Zr alloy (upper half) and Mg-1.4wt%CaO alloy (lower half) at different positions in the ingot cast in the V-shape copper mould.](image)

In the Mg-1.0wt%Zr alloy, the average grain size decreased from 81.7 μm at position C to 42.3 μm at position A2. Similarly, in the Mg-1.4wt%CaO alloy, the average grain size reduced from 106.7 μm at position C to 66.25 μm at position A2. However, at positions A1 in both alloys, where the highest cooling up to 36°C/sec at the tip of the ingots was achieved, grain coarsening occurred. In the Mg-1.0wt%Zr alloy, the average grain size at position A1 was increased to 77 μm from 42.3 μm at position A2 where the cooling rate was relatively lower. Similarly, in the Mg-1.4wt%CaO alloy, the average grain size at position A1 is 113.76 μm, which is much larger than the grain size of 66.2 μm at position A2.

In order to investigate and understand the combined effects of cooling rate with solute addition, different amounts of Zn and Al solutes were added to Mg melts so that the Q-values of the solutes in the melt were kept at 5 and 12 K. It is worth mentioning that these particular solutes were deliberately chosen because their Q-values at concentration of 1.0wt% in Mg (Q_{Zn}=5.31 K and Q_{Al}=4.32 K) are very close. At Q = ~5 K, in the whole ingots of both alloys, finer grains were
obtained at the mould tip (position A), where cooling rate is the highest, than those obtained at position B that was associated with slower cooling. For the Mg-Al alloy, as shown in Fig. 4, average grain size decreased from 427.6 μm at position B to 338.2 μm at position A at the tip of the mould. Similarly, as can be seen in Fig. 5, the average grain size of the Mg-Zn alloy decreased to 323.2 μm at position A, from 585 μm at position B. At higher Q-value of ~12 K, in the Mg-Zn alloy, higher cooling rate corresponded to finer grains. As shown in Fig. 5, the average grain size was decreased from 408.9 μm at position B to 268.2 μm at position A. However, in the Mg-Al alloy, although in the major part of the ingot, finer grains were obtained at the positions associated with higher cooling rate, grain coarsening occurred at the tip of the ingot, where the cooling rate is the highest. As can be seen in Fig. 4, the average grains size at position A1 was increased to 125.6 μm from 78.6 μm at position A2.

Fig. 4 Typical polarized light microscopy micrographs for the tip and middle parts of the V-shaped ingot of as-cast Mg-Al alloys at different Q values (~ 5 K and ~12 K).
Fig. 5 Typical polarized light microscopy micrographs for the tip and middle parts of the V-shaped ingot of as-cast Mg-Zn alloys at different Q values (~ 5 K and ~12 K).

The effect of cooling rate on the measured grain size for all alloys is shown in Fig. 6. It can be seen that increasing the cooling rate led to finer grains in Mg-1.2wt.%Al (Q = ~5 K), Mg-1.0wt.%Zn (Q = ~5 K) and Mg-2.3wt.%Zn (Q = ~12 K). However, in Mg-1.4wt%CaO, Mg-1.0wt.%Zr and Mg-2.8wt.%Al alloys, grain coarsening occurred at the mould tip where the cooling rate was the highest. Furthermore, comparison of the Mg-2.8wt.%Al and Mg-2.3wt.%Zn alloys indicates that, although both have the same Q-value of ~ 12 K, grain coarsening only occurred in the Mg-2.8wt.%Al alloy at high cooling rate. In the Mg-2.3wt.%Zn alloy finer grains are observed at the mould tip. These results suggest that, even the Q-values are the same, the grain size of the as-cast Mg alloys depends strongly on the type of solute added and also the cooling rate. A question arisen is why the grain coarsening only occurred in the Mg-Al alloy, but not in the Mg-Zn alloy?
Recent work by Fan and co-workers [34] found that, pure Mg showed better grain refinement results than Mg-1.0wt.%Zr alloy at enhanced cooling conditions such as that associated with high pressure die casting (HPDC). Two key factors were believed to be taking the responsibility for the large grains in the Mg-1.0wt%Zr alloy. One was the low number density of Zr particles compared to MgO in the melt, and another was the latent heat released from the initially nucleated grains on Zr nucleants, which inhibited the nucleation on MgO particles [34]. However, there was still lack of direct experimental evidence verifying the nucleation occurred on MgO particles. In the present result, the grain size at the tip (fast cooling condition) of the pure Mg ingot (Fig. 2) is still much coarser than that of the other alloys (Figs. 3 and 4). Furthermore, in a study by Johnsson [26], grain coarsening was observed in Al alloys containing over 3.0wt%Si at higher cooling rate. Johnsson considered that at high cooling rate the capillary effects were more important than the solute effects. Thus, the grains were coarsened. However, such grain coarsening resulted from the fast cooling in Al alloys differed from the present work. First, increasing Si content over 3.0wt.% in Al alloys leads to grains poisoning effect [37-39]. But, none of the solutes used poisons the cast Mg alloys. Second, reaction between Si and Ti may have weakened the grain refining effect by lowering the solutes concentrations in the melt [26]. Hence, neither Fan’s assumption nor Johnsson’s hypothesis can be directly used to explain the present results.

Previous work [22, 24, 25] has verified that addition of either Zr or CaO into Mg melt introduces both solutes (Zr and Ca) with high Q-values and effective nucleants (Zr and CaO particles) because Zr can be partially dissolved into the Mg melt and the remaining Zr particles can
act as nucleants and CaO can be partially reduced by Mg forming Ca and un-reduced CaO particles act as nucleants. Hence, solidification of both Mg-1.0wt%Zr and Mg-1.4wt%CaO alloys were associated with the formation of constitutional undercooling zone. Thus, the potential of heterogeneous nucleation within the constitutional undercooling zone is high. However, the formation of constitutional undercooling zone depends on both the solute segregation and the actual temperature gradient at front of the growing solid/liquid interface [32, 40, 41]. Hence, for a particular alloy, there are two factors that affect the constitutional undercooling zone in the condition of fast cooling. One is the temperature gradient and another is the actual melting temperature distribution ahead of the solid/liquid interface. Using the same hypothetical constitutional undercooling representation in reference [40], Fig. 7 has been created. It schematically illustrates the relation between the temperature gradient and the distribution of liquidus temperature at the front of the solid/liquid interface. The two straight lines (TG1 and TG2) represent the temperature gradients. Because fast cooling normally corresponds to higher temperature gradient, TG1 is for fast cooling and TG2 for slow cooling. If we assume the effect of cooling rate on solute segregation is ignorable, the distribution of the actual melting temperature of the liquid at front of the growing solid/liquid interface would be the same for both fast and slow cooling. In Fig. 7, Tl represents the variation of the actual melting temperature at front of the solid/liquid interface as a result of rejection of solutes from the solid. It can be seen that at fast cooling, which corresponds to the TG1, smaller constitutional undercooling zone (the red shadowed area) would be generated compared with the TG2, which corresponds to the slow cooling and creates larger constitutional undercooling zone (the hatched area). But, according to the Interdependency theory [33], there is a nucleation free zone (nfz) as represented by xnfz in Fig. 4 at front of the growing solid/liquid interface. Within this nucleation free zone, even constitutional undercooling zone forms, but no nucleation would occur. In this case, the constitutional undercooling would simply promote the growth of grains. Hence, it is reasonable to hypothesize that, for an alloy refined by both solutes and inoculants, there is a critical cooling rate, over which the size of the constitutional undercooling zone formed is less than the xnfz due to the large TG. As a result, the undercooling will enhance the growth rate of previously nucleated grains because no “suppressors” (new grains) formed within the constitutional undercooling zones to supress their growing.
Fig. 7 Schematic drawing represents the effect of cooling rate and solute on the constitutional undercooling formation ahead of the S/L interface.

On the other hand, grain refinement in Mg-Al and Mg-Zn alloys is mostly dominated by the effect of solutes in suppressing the grain growth. Solute addition results in the formation of constitutional undercooling zone at front of the growing solid/liquid (S/L) interface in an alloy. When the constitutional undercooling zone is “big” enough, subsequent nucleation within the constitutional undercooling zone can suppress the further growth of the existing grains, leading to grain refinement [33]. However, the establishment of constitutional undercooling zone that is “big” enough to promote further nucleation depends on atomic diffusion, which is related to cooling rate (temperature of diffusion) and the diffusivity of solutes in solid Mg. At very high cooling rate, as at the tip of the cooper V-shape mould, the establishment of the constitutional undercooling zone can be delayed due to the low diffusivity of solute atom in solid, because the solidification starts at lower temperatures when the cooling rate is high. Such delay allows more time for the existing grains to grow larger. Thus, grain coarsening occurs. Furthermore, a recent study suggested that the diffusion coefficient of Zn in Mg is higher than that of Al at the same temperature used in the current work [42]. Hence, during solidification, Zn has higher ability to rapidly establish a “big” enough constitutional undercooling ahead of the S/L interface, promoting the further heterogeneous nucleation that eliminated the growth of existing grains. As a result, grain refinement was obtained, even at the tip of the ingot. In the Mg-Al alloy, due to the lower diffusivity of Al in solid Mg compared with Zn, some delay in establishment of the “big” enough constitutional undercooling for heterogeneous nucleation might occur, which allowed the existing grains to continue growing when the cooling rate is high enough. Therefore, grain coarsening happened at the tip of the ingot of the Mg-Al alloy. The same as the above argument, it is considered that there is a critical cooling rate for each alloy. When the cooling rate is greater than this critical cooling rate value, grain coarsening may occur. For the Zn addition in Mg, such cooling rate may have not been reached in the present
work. The concept of ‘critical cooling rate’ proposed here is used to qualitatively describe the cooling rate effect on grain refinement of cast alloy. However, it is hard to accurately determine such critical cooling rate using the presently available casting facilities for all alloys. For Mg-1.0wt.%Zr, Mg-1.4wt.%CaO and Mg-2.8wt.%Al alloys, it lies between 29.5 and 36.79°C/sec. For all other alloys, the critical cooling rate may be over 36.79°C/sec, which is highest cooling rate we could achieve. Currently, further work is being undertaken to verify this hypothesis in other alloy systems and trying to more accurately determine such critical value for more alloys.

4. Conclusions:

The present work indicated that fast cooling does not always lead to grain refinement during solidification of magnesium alloys. When the cooling rate was over a critical cooling rate, grain coarsening occurred in both the Mg-1.0wt%Zr, Mg-1.4wt%CaO and Mg2.8wt%Al alloys. Such grain coarsening is likely attributed to either the size reduction in constitutional undercooling zone due to the higher temperature gradient at fast cooling or the slow solute atom diffusion rate occurred at lower temperatures.

5. References:

35. MATLAB R2013b, 2013, MathWorks Inc. Natick, MA, USA.


Chapter 6: Various solutes additions to Mg-Al based alloys

6.1 Chapter overview:

The previous chapters in this PhD thesis concentrated on the effect of solutes and/or inoculants on the microstructure of Al free Mg alloys. However, the majority of commercially used Mg alloys are Mg-Al based such as the well-known AZ and AM series. But, Mg-Al alloys suffer from poor mechanical properties due to the precipitation of $\text{Mg}_17\text{Al}_{12}$ intermetallic on the [0001] basal plane which is also a slip plane in HCP structure. In order to overcome this setback, two strengthening methods are widely used. They are grain refinement and precipitation hardening by precipitates formed on the non-basal planes. By looking in the literature, limited reports were found studying the effect of tertiary elements on microstructure of Mg-Al based alloys. Hence, in this chapter, the effects of various tertiary solutes addition to Mg-Al based alloys are investigated in terms of grain refinement and hardness. Also, the effects of heat treatment on the hardness and microstructure of selected alloys are highlighted. The results should help in understanding the role of various elements when added to Mg-Al base alloys which can be used as a reference for designing new grain refiners.

Titanium, silicon, manganese, copper, calcium solutes were added, separately, to Mg-3Al and Mg-9Al base alloys through casting. Hardness and microstructures were used to evaluate the alloys. Results showed that the effect of Ti, Sn or Mn additions to Mg-Al base alloys is not very significant in terms of grain refinement and/or hardness improvement. Thus, further solution treatment and aging experiments were then designed and performed on Si, Cu and Ca containing alloys. Following that, microstructures and hardness were examined for the heat treated alloys. Analysis of the results suggested that only Ca containing Mg-3Al base alloy showed precipitation hardening effect, which might be attributed to the presence of Ca containing intermetallic compounds. On the other hand, $\text{Mg}_17\text{Al}_{12}$ intermetallic played a major role in precipitation hardening of all Mg-9Al based alloys, which in return, enhanced the hardness of the alloys. The major content of the present work was in the Paper 5 that was published in Magnesium Technology 2017, Springer International Publishing, in 2017; Page 259-267 with a title “Effect of solutes additions on the microstructure and mechanical properties of cast Mg-Al based alloys”.

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6.2 Associated paper:

PAPER 5

Effect of solutes additions on the microstructure and mechanical properties of cast Mg-Al based alloys

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Effect of solutes additions on the microstructure and mechanical properties of cast Mg-Al based alloys

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Abstract

The effects of tertiary solute additions on the microstructure and mechanical properties of Mg-Al based alloys were studied in this chapter. Titanium, silicon, manganese, copper, calcium and tin were added separately to Mg-3.0wt.%Al and Mg-9.0wt.%Al alloys with various addition levels. The as-cast grain sizes and hardness were then measured. Further solution treatment and aging were performed on selected alloys followed by microstructure examination and hardness test. In terms of microstructure, results showed that even though higher Q-values can be obtained through increasing the solutes addition, grain refinement is not always associated with the Q-values. In addition, intermetallic compounds played a major role in enhancing the hardness of the alloys.

Keywords: Casting, Mg alloys, Mechanical properties, Ternary alloys.

List of abbreviations:

HPDC: High pressure die casting
E2EM: Edge-to-Edge Matching Model
Q-value: Growth restriction factor.
Temp.: Temperature.
TEM: Transmission electron microscope.
1. Introduction:

Nowadays, most commonly used cast Mg alloys are Mg-Al based, including AM and AZ series, which predominantly used as high pressure die casting (HPDC) and non-HPDC [1]. These alloys are used in automotive and aerospace industries [2-4] due to their lightness and high castability. However, these types of alloys are associated with low ageing response due to the formation of Mg$_{17}$Al$_{12}$ intermetallic compound on the basal slip plane of HCP Mg. The low strength has limited their wider applications. In order to overcome this problem, grain refinement, solid solution strengthening and precipitation hardening have shown success in improving the mechanical properties of as-cast Mg-Al based alloys.

Although grain refinement can be achieved through many techniques, inoculation has been a well-known method due to many aspects such as ease of application [5]. A single model to describe the grain refinement mechanism by inoculation has not been found yet. However, it has been widely accepted that the process is dominated by two main factors, i.e., the presence of solute elements, which restricts the growth of formed grains, and potent heterogeneous nucleation sites that promote the nucleation. The solute effect can be described by the Q-value, which is related to the undercooling (\(\Delta T\)) produced at the solid/liquid (S/L) interface during alloy solidification. In binary system, Q can be described by the equation \(Q = mC_0(K-l)\), where \(m\) is the slope of the liquids line, \(C_0\) is the solute composition, in wt.% in the alloy and \(K\) is the equilibrium partitioning coefficient. However, in ternary systems the calculations are more complicated and can be found in reference [6]. On the other hand, crystallographic models, such as the edge to edge matching (E2EM) model, [7, 8] have been highly effective in predicting the potency of nucleating particles such as Al$_2$Y, CaO and ZnO in Mg systems [9-11]. Using these two factors, many new grain refiners have been discovered and reported in the literature for Mg-Al bases alloys. Among them, SiC [12], Al$_2$Y [9] and Al$_4$C$_3$ [13], are the typical examples. However, none of these grain refiners is as efficient as Zr in non-Al/Mn/Si containing Mg alloys. Even increasing the Q-value of the melt through addition of tertiary alloying element, such as Zn in AZ series, it was not as successful as Zr in terms of grain refinement.

Precipitation hardening is another well-known strengthening mechanism for Mg alloys. This is normally achieved through heat treatment, which includes solution treatment at relatively high temperature, followed by quenching to create a supersaturated solid solution and artificial ageing at an intermediate temperature [14]. To increase the ageing response of the Mg-Al alloys, a tertiary solute can be added. The AZ series and AM series alloys are the most successful examples. In the present work, six different tertiary solutes, , titanium, silicon, manganese, copper, calcium
and tin were added to the Mg-3wt.%Al and Mg-9wt.%Al based alloys to investigate their influence on the microstructure and ageing responses.

2. Experimental procedures:

2.1. Casting:

Commercial purity Mg, Al, Cu, Sn, Mn pure metal ingots or pieces, Mg-9.0wt.%Ca, Al-50.0wt.%Si and Al-6.0wt.%Ti master alloys were used as raw materials to prepare various alloys. Melting was performed in an electric resistance furnace using boron nitride coated steel crucibles. Temperature was set at 730°C for melting. To protect the melt from reacting with the surrounding air, a mixture of 1% SF6–49%CO2–50% dry air cover gas was used as protective gas. First, Mg and Al ingots were melted, then metal chips or master alloys were added, followed by manually stirring for 30 seconds. Then the melt was isothermally held for various times depending on the alloys. The holding time was 20 minutes for Ca, Mn and Ti containing alloys, 30 minutes for Cu and Sn containing alloys and 60 minutes for Si containing alloys to ensure that all additives were fully dissolved. Compositions of all cast alloys in this study are listed in Table 1. After stirring, melts were set to rest for 5 minutes prior to casting. Melts were then poured into 200°C preheated cylindrical steel moulds with conical shaped ingot cavity. A schematic drawing for the cast ingots is shown in Fig.1.

Table 1: Addition levels, in wt.%, of solutes to Mg3.0wt%AlX and Mg9.0wt%AlX alloys.

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
<th>X4</th>
<th>X5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>1.5</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>7</td>
</tr>
<tr>
<td>Cu</td>
<td>0.25</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>-</td>
</tr>
<tr>
<td>Ca</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Sn</td>
<td>0.5</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>Mn</td>
<td>0.1</td>
<td>0.2</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
</tr>
<tr>
<td>Ti</td>
<td>0.02</td>
<td>0.03</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
</tr>
</tbody>
</table>
2.2. Microstructure Examination:

Samples were cut from the ingots, then were mounted, polished and etched for microstructure examination using two different etching solutions. For secondary phase examination, 15% Nital was applied for 1.5 seconds then samples were examined under the optical microscope. To reveal the grains, an etchant consisting of 2.5 g picric acid, 50 ml ethanol, 2.5 ml acetic acid and 5 ml distilled water was used with 5 seconds etching. Polarized light optical microscope was used to examine the grains. Grain sizes were measured using the linear intercept method [15].

2.3. Hardness:

For hardness testing, samples were cut, mechanically ground using SiC sand papers then a Leco LV800 AT micro Vickers hardness tester was used. The test was performed through applying a 5 kg load on the diamond indenter for 10 seconds. 10 readings were taken from each sample to ensure results reliability.

2.4. Heat Treatment:

Selected alloys were heat treated. The solid solution treatment and ageing temperatures and times are listed in Table. 2.
Table 2: Alloys compositions, solution treatment and aging temperatures and times for selected samples.

<table>
<thead>
<tr>
<th>Tertiary Solute added</th>
<th>Alloy composition</th>
<th>Sol. treatment</th>
<th>Aging</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Temp. (°C)</td>
<td>Temp. (°C)</td>
</tr>
<tr>
<td>Si</td>
<td>Mg3.0wt.%Al3.0wt.%Si</td>
<td>480</td>
<td>180</td>
</tr>
<tr>
<td></td>
<td>Mg9.0wt.%Al3.0wt.%Si</td>
<td>420</td>
<td></td>
</tr>
<tr>
<td>Cu</td>
<td>Mg3.0wt.%Al3.0wt.%Cu</td>
<td>480</td>
<td>24</td>
</tr>
<tr>
<td></td>
<td>Mg9.0wt.%Al3.0wt.%Cu</td>
<td>420</td>
<td>180</td>
</tr>
<tr>
<td>Ca</td>
<td>Mg3.0wt.%Al5.0wt.%Ca</td>
<td>480</td>
<td>200</td>
</tr>
<tr>
<td></td>
<td>Mg9.0wt.%Al0.5wt.%Ca</td>
<td>420</td>
<td>180</td>
</tr>
</tbody>
</table>

3. Results and discussion:

3.1. The effects of solutes additions on the microstructures and hardness of the as-cast alloys:

3.1.1 Silicon

Fig. 2 (a - c) show the optical micrographs of as-cast Mg-3.0wt.%Al alloy with various Si additions. From the micrographs it can be seen that addition of 2 to 7 wt%Si to the base alloy led to grain coarsening. The average grain size was increase from ~ 139 µm for the base alloy to ~ 173µm with 3.0 wt.% Si addition. Further addition of Si solute had no noticeable effect on the grains size as shown in Fig. 2 (c). The same coarsening effect by Si addition was also observed in the Mg-9.0wt.%Al base alloy. Figs. 2 (d and e) show that 2.0 wt.% Si addition to the base alloy led to increasing the average measured grain size from ~ 97µm to ~ 140µm. Similar with the Mg-3.0wt.%Al based alloys, further addition of Si solute had no effect on the grains size.

Fig. 2: (a-c) typical optical micrographs of the as-cast Mg-3.0wt.%Al alloys with different Si addition levels (a) base alloy, (b) 2.0 wt.% Si and (c) 7.0 wt.% Si. (d-f) typical optical micrographs ofhe as- cast Mg-9.0wt.%Al alloys with different Si addition levels (d) base alloy, (e) 3.0 wt.% Si and (f) 7.0 wt.% Si
The variation of average grain sizes of all alloys with Si addition is plotted in Fig. 3 (a). It can be noted that increasing the addition level of Si solute led to a significant grain coarsening in both alloys. However, the grains sizes remained almost constant with increasing Si contents above a particular concentration (3.0 wt.% for Mg-3.0wt.%Al and 2.0wt.% for Mg-9.0wt.%Al). This suggests the potential of a threshold level of Si addition, after which no effect will be found on grains size in Mg-Al base alloys. In addition, the limitation of casting conditions might also restrict the dissolution of the full amounts of Si at higher addition level. For instance, from the Mg-Si binary phase diagram [16], it can be noted that the maximum concentration of Si to dissolve in the Mg melt at 730°C is 3.0 wt.%. Similarly, due to the lower concentration of Si in Mg-9.0wt.%Al based alloys, less Si could be dissolved at the same temperature. Hence, the amount of maximum Si dissolved in the melt was less (2.0 wt.%). Hence, the existence of a threshold level of Si addition is related to the solubility of Si in the Mg melt at the used casting temperature of 730°C.

Although the fact that Si addition leads to grains coarsening is still yet discussed, previous research [6] indicated that addition of a tertiary element to a binary alloy should lead to the increase in the Q-value in the system, which in return leads to finer grains. However, it has been confirmed that the grain growth restriction is not the only factor controlling the grain refinement process [5, 17, 18]. Other parameters, such as the presence of potent nucleation sites which increase the potential of heterogeneous nucleation, the chemical nature of the melt and the kinetics of the solidification reaction [5, 19], are found to directly influence the final grain size. In terms of the Mg-Al-Si ternary phase diagram, it can be noted that the Mg$_{17}$Al$_{12}$ and Mg$_2$Si intermetallic compounds are expected to form at all concentrations used in this study [20]. It has been previously confirmed that formation of intermetallics reduces the concentration of solutes during solidification which in return weakens their ability to refine the grains [10]. But, none of the two intermetallics formed can be directly related to the grain coarsening. Lee et. al. [21] reported that addition of Si
into pure Mg in very small amounts of up to 0.15wt%Si led to effective grain refinement but above this addition no further grain refinement could be obtained. At present, the minimum concentration of Si added was far above the limit of that reported in [21]. However, combining the current results with those reported in [21], leads to a very interesting conclusion that Si might have the same poisoning effect found in Al-Si alloys [22] with Mg alloys but this conclusion needs further in-depth study to confirm it.

On the other hand, Si addition to Mg-Al base alloys led to increasing hardness values as shown in Fig. 3 (b). These results come in contrast with the grain coarsening found with Si additions which should lead to softer alloys. But, this increase is highly likely due to the formation of the hard Mg$_2$Si and Mg$_{17}$Al$_{12}$ intermetallic compounds. Interestingly, the same behaviour was found in both microstructure and hardness results. When the Si additions were over 3.0 wt.% in the Mg-3.0wt.%Al and 2.0 wt.% Si in the Mg-9.0wt.%Al base alloys, hardness values remained constant and no change was found with increasing Si addition levels. These results further support the claim that above these concentrations no more Si could be dissolved during casting, but Si remained as inclusions.

3.1.2. Tin:

In Fig. 4 (a and b), the optical micrographs show slight grain refinement at small addition levels of Sn into Mg-3.0wt.%Al base alloy. Best grain refinement obtained was at 1.0 wt.% Sn with average grain size of ~ 207.37 $\mu$m which is only ~ 7 % smaller than that of the base alloy (223.1 $\mu$m). With increasing the addition level of Sn over 2.0 wt.%, grain coarsening was obtained as shown in Fig. 4 (c) and the average grain size was ~ 258.8 $\mu$m. Similarly, the effect of Sn on the grains of Mg-9.0wt.%Al base alloys was minor. Micrographs in Figs. 4 (d-f) show that the average grain size was increased from ~ 113.55 $\mu$m, for the base alloy, to ~ 148.79 $\mu$m with 2.0 wt.% Sn addition. Further addition led to slight coarsening and the average grains size was ~ 150.5 $\mu$m with 5.0 wt.% Sn addition. In Fig. 5 (a) the relationships between the grains size and the solute addition levels are plotted for both alloys. From the results, it can be noted that Sn performed the same as Si in the Mg-Al alloys in terms of the grain refinement. Finer grains were obtained with lower concentrations of the solute then grain coarsening took place with higher addition levels, likely due to the poisoning effect. Even though Sn has been widely used in Mg alloys for creep resistance purposes [5, 14], no reports could be found in the literature supporting the current claim. Also, the results in the current study are not enough to fully understand this behaviour. However, a separate in-depth study in this system is highly likely to come up with interesting results.
Unlike microstructure, hardness showed a linear increase with increasing the addition levels of Sn solute to both Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys as shown in Fig. 5 (b). This increase in hardness is highly likely due to the formation of intermetallic compounds such as Mg$_2$Sn and Mg$_{17}$Al$_{12}$.

### 3.1.3. Copper:

Unlike Si and Sn, grain refinement was obtained in Mg-3.0wt.%Al based alloys with the addition of Cu solute. As-cast optical micrographs in Figs. 6 (a and b), show that 1.0wt.% Cu led to
significant drop in the grain size from ~162.1 μm, for the base alloy, to ~104.6 μm. With further Cu addition to 3.0wt%, as shown in Fig. 6(c), slight decrease in the grains size was obtained. The measured grain size was ~117.1μm. Similarly, grain refinement was also obtained with Cu addition to Mg-9.0wt.%Al base alloys. The average grain size was reduced from ~94.3 μm for the base alloy, in Fig. 6 (d), to ~82.2 μm for Mg-9.0wt.%Al-3.0wt.%Cu in Fig. 6 (f). Even though, the grain refinement results cannot be considered significant, plots of grains size vs. solute concentration in Fig. 7 (a) strongly suggest that more addition of Cu leads to higher grain refining efficiency.

The current results come in agreement with results found in the literature when Cu was added to Mg alloys [23, 24] and finer grains were obtained. However, the role of Cu in Mg alloys grain refinement has not been extensively studied in these reports for two reasons. One, only slight grain refinement was obtained with Cu addition. Second, and more importantly, addition of Cu leads to the formation of Mg2Cu intermetallic compound, which is directly related to reduction of alloy’s formability and corrosion resistance. Thus, the grain refinement could be attributed to either the heterogeneous nucleation on the in-situ formed nucleants during solidification or the effect of Cu as a solute in restricting grains growth or both. In order to clarify the possible grain refinement mechanism, crystallographic matching between the α-Mg and the intermetallics were calculated using the Edge to edge (E2EM) matching model. Results in Table 3 showed potential orientation relationships between one of the intermetallics, Al2Cu, and Mg matrix. However, due to either the large interatomic spacing misfit along the matching directions or the high interplanar mismatch values nucleation of α-Mg on Al2Cu particles was less likely. Instead, the role of Cu as a solute can be considered as the main factor that contributed to the grain refinement.
Table 3: Misfit and mismatch (<10%) of matching rows and planes calculated using E2EM model between BCT-Al$_2$Cu and HCP-Mg phases

<table>
<thead>
<tr>
<th>Rows</th>
<th>Planes</th>
<th>Possible ORs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>Al$_2$Cu</td>
<td>$f_r$</td>
</tr>
<tr>
<td>[111]</td>
<td>[11][13]</td>
<td>8.24%</td>
</tr>
</tbody>
</table>

Hardness values in Fig. 7 (b) come in agreement with the microstructure and increasing Cu contents led to higher hardness values of the alloys. Although grain refinement is believed to increase hardness of the metal, the increase was marginal because of the slight reduction in grains size obtained. Thus, it is highly likely that the formation of intermetallic compounds during solidification strongly contributed to the hardness of the alloys.

3.1.4. Calcium:

Due to the relatively high Q-value of Ca in Mg [1], Mg-Al-Ca has been one of the most comprehensively studied systems in the literature. Micrographs in Figs. 8 (a-c) show the evolution of as-cast microstructure in Mg-3.0wt.%Al base alloy with Ca additions. With 2.0 wt.% Ca addition, the average grains size increased from ~ 154.5 μm, for Mg-3.0wt.%Al, to ~245.9 μm. Further coarsening occurred, leading to a grain size of ~ 281.3 μm with 5.0 wt.% Ca addition. Similar results were obtained in Mg-9.0wt.%Al base alloys as shown in Figs. 8 (d-f). The average grains size of the base alloy was ~ 115.6 μm. But with 2.0 wt.% Ca addition, the grains were coarsened to ~ 335.2 μm. More Ca addition led to further coarsening and the final grain size reached ~ 348.6 μm at 5.0 wt.% addition level. The coarsening behaviour can be clearly seen in plots of the average grains size of all alloys versus solute addition levels in Fig. 9 (a). Ca solute
reacts in a similar way to Cu when added to Mg-Al based alloys. But Ca has higher tendency to form intermetallic compounds with Al over Mg. This reaction forms Al2Ca intermetallic compound, which reduces the concentration of both solutes in the melt. As a result both solutes effects on grain refinement are weakened, resulting in the grain coarsening. However, by looking at the current results, even though both solutes dilute each other, equiaxed grains structure is still presented. It has been previously proven that Al2Ca has good crystallographic matching with Mg matrix, thus it was highly likely that the Al2Ca acted as heterogeneous nucleation sites for the matrix. This is most likely what prevents the formation of columnar grains even if most atoms of both solutes were consumed to from Al2Ca intermetallics.

Fig. 8: (a-c) Typical micrographs for as-cast Mg-3.0wt.%Al alloy with different Ca addition levels (a) base alloy, (b) 2.0 wt.% Ca and (c) 5.0 wt.% Ca. (d-f) Typical metallographs for as-cast Mg-9.0wt.%Al alloy with different Ca addition levels (d) base alloy, (e) 2.0 wt.% Ca and (f) 5.0 wt.% Ca.

Mg-3.0wt.%Al based alloys showed increase in hardness with Ca addition as shown in Fig. 9 (b). These results come in contrast with the grains coarsening obtained and presented through the microstructure results. Similar behaviour was obtained at the Mg-9.0wt.%Al base alloys and, addition of 0.5 wt.% Ca solute led to a significant increase in hardness. But further addition did not have any noticeable effect on the hardness values. It is obvious that Ca addition has a positive effect on the hardness of Mg-Al base alloys, which was highly likely due to the formation of hard intermetallic compounds, such as Mg2Ca and Al2Ca. Also solid solution strengthening due to the Ca solute presence might has a positive effect on the hardness of the alloys.
Fig. 9: (a) Relationships between grains size and wt.% of Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys with various addition levels of Ca. (b) Relationships between hardness (HV) and wt.% of Mg3.0wt.%Al and Mg9.0wt.%Al base alloys with various addition levels of Ca.

3.1.5. Titanium:

Despite the fact that Ti has almost no solubility in Mg alloys [5], some controversies in the literature on the effects of Ti addition on Mg alloys microstructures are still standing. In the current results, optical micrographs in Fig. 10 (a-c) show that minor grain coarsening was obtained with Ti addition to Mg-3.0wt.%Al based alloys. Plots of the measured grains size with solute addition, in Fig. 11 (a), show that grains of Mg-3.0wt.%Al base alloy were coarsened from ~ 99.2 μm to ~ 104.3 μm with 0.05 wt.% Ti addition to the base alloy. Further addition led to more coarsening and the largest grains size of ~ 111.5 μm was obtained at 0.1 wt.% Ti addition. Similar results were obtained with Ti addition to Mg-9.0wt.%Al base alloys as shown in Fig.10 (d-f). But the coarsening was more significant than that obtained with Mg-3Al base alloys. Grains were coarsened from ~ 68 μm for the base alloy to ~ a maximum of ~ 95 μm at 0.3 wt.% Ti addition after which grains size remained constant with further Ti addition. By looking at the results, it can be noted that even though addition of Ti into Mg-Al base alloys led to grain coarsening, the coarsening effect was not very significant and can be considered minor, which further supports the claim that Ti is very hard to dissolve into Mg melts.
Fig. 10: (a-c) Typical micrographs for as-cast Mg-3.0wt.%Al alloy with different Ti addition levels (a) base alloy, (b) 0.05wt.% Ti and (c) 0.15wt.% Ti. (d-f) Typical metallographs for as-cast Mg-9.0wt.%Al alloy with different Ti addition levels (d) base alloy (e) 0.05 wt.% Ti and (f) 0.15 wt.% Ti.

Fig. 11 (b) show the effect on hardness of Ti solute addition to both base alloys and it can be seen that there is almost no change in hardness with the addition of Ti except for 0.02 wt.% Ti addition to Mg-9.0wt.% base alloy which highly likely is due to an experimental error. The results come in agreement with the minor changes in grains size obtained with Ti addition and shown above.

Fig. 11: (a) Relationships between grains size and wt.% of Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys with various addition levels of Ti. (b) Relationships between hardness (HV) and wt.% of Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys with various addition levels of Ti.

3.1.6. Manganese:

So far, even though grain coarsening was the general trend for most alloys, no transformation in grains structure has occurred; but in Mg-Al-Mn ternary system, this was not the case. Fig. 12, shows the effect of various Mn addition levels on the two base alloys, Mg-3.0wt.%Al
and Mg-9.0wt.%Al. Grains were significantly coarsened with 0.5 wt.% Mn addition, in Fig. 12 (b), than those of the base alloy in Fig. 12 (a). Increasing the addition level led to transforming the grain structure from equiaxed to columnar at 0.5 wt.% Mn in Mg-3.0wt.%Al base alloy as shown in Fig.12 (c). Similar behaviour was found in Mg-9.0wt.%Al base alloy, but columnar grains were obtained at 1.5wt.% Mn addition level as plotted in Fig. 13 (a). Unlike other solutes which tend to form intermetallic compounds with Mg, Mn act in a similar fashion to Ca when added to Mg-Al alloys as it has higher affinity to react with Al solute rather than Mg [6]. Thus, in both ternary alloys Mg-Al-Ca and Mg-Al-Mn, significant grain coarsening was found due to the consumption of the two solutes in the melt. While Al$_2$Ca might have contributed in reserving the equiaxed grain structure in Mg-Al-Ca ternary system [10], absence of potent nucleants in addition to solutes consumption in the current system led to the formation of columnar grains with increasing Mn addition levels. Although the Al$_8$Mn$_5$ might form in the Mg-Al-Mn system, it has been crystallographically verified as a non-effective nucleant [25].

![Fig.12: (a-c) Typical micrographs for as-cast Mg-3.0wt.%Al alloy with different Mn addition levels (a) base alloy, (b) 0.2wt.% Mn and (c) 0.5wt.% Mn. (d-f) Typical metallographs for as-cast Mg-9.0wt.%Al alloy with different Mn addition levels (d) base alloy, (e) 1.0wt.% Mn and (f) 1.5wt.% Mn](image-url)

Unlike all other alloys, addition of Mn led to decreasing the hardness of the alloys as plotted in Fig. 13 (b). These results come in agreement with the grains structure transformation from equiaxed to columnar. However, if the loss of both solutes comes from the reaction of Mn and Al to form intermetallic compounds, why did these intermetallic compounds not increase the hardness of the alloys? Hence, more studies need to be done to further investigate this system.
Fig. 13: (a) Relationships between grains size and wt.% of Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys with various addition levels of Mn. (b) Relationships between hardness (HV) and wt.% of Mg-3.0wt.%Al and Mg-9.0wt.%Al base alloys with various addition levels of Mn.

3.2. Effect of the heat treatment

By comparing all hardness and microstructure results, it was found that Sn, Ti and Mn containing alloys suffer from poor hardness and grain coarsening. Thus, there was no significance for continue study on the heat treatment. On the other hand, alloys with higher hardness were chosen for further solution treatment and ageing. Compositions of the alloys were Mg-3.0wt.%Al, Mg-3.0wt.%Al-3.0wt.%Si, Mg-3.0wt.%Al-3.0wt.%Ca and Mg-3.0wt.%Al-3.0wt.%Cu, Mg-9.0wt.%Al, Mg-9.0wt.%Al-3.0wt.%Si, Mg-9.0wt.%Al-3.0wt.%Cu and Mg-9.0wt.%Al-0.5wt.%Ca.

Fig. 14 (a and b) shows the ageing curve for Mg-3.0wt.%Al and Mg-9.0wt.%Al based alloys. In Fig. 14 (a), hardness values at 0 aging time (as-solution treated samples) for the Mg-3.0wt.%Al-3wt.%Si and the Mg-3.0wt.%Al-3.0wt.%Cu alloys were higher than that of the base alloys. All three alloys shared the same hardness trend with ageing time and noticeable change in hardness for the three alloys. The peak age for the Mg-3.0wt.%Al-3.0wt.%Ca was achieved at 5 hours ageing. Further ageing led to lowering the hardness. In Fig. 14 (b), the hardness of all Mg-9.0wt.%Al based alloys showed precipitation hardening behaviour; i.e. hardness increased with increasing ageing time. Also, Mg-9.0wt.%Al, Mg-9.0wt.%Al-3.0wt.%Si and Mg-9.0wt.%Al-3.0wt.%Cu alloys shared the same trend as in the three alloys, peak hardness level was reached at 48 hours beyond which no noticeable hardness increase could be seen.
Fig. 14: Relationships between hardness (HV) and ageing time for selected samples. (a) Mg-3.0wt.%Al, Mg-3.0wt.%Al-3.0wt.%Si, Mg-3.0wt.%Al-3.0wt.%Cu and Mg-3.0wt.%Al-5.0wt.%Ca. (b) Mg-9.0wt.%Al, Mg-9.0wt.%Al-3.0wt.%Si, Mg-9.0wt.%Al-3.0wt.%Cu and Mg-9.0wt.%Al-0.5wt.%Ca.

In order to understand the hardness results in Fig. 14, samples were further investigated in optical microscope to reveal the change in microstructures and intermetallic compounds before and after aging and the results are shown in Fig. 15. The most as-solution treated samples showed incomplete melting of the intermetallic compounds as shown in Fig. 15(A). However, the microstructure of the base alloys in Fig. 15 (A1 and A5) showed no presence of Mg_{17}Al_{12} intermetallic. Hence, it is quite obvious that the slight increase in hardness, of the as solution treated ternary alloys compared with the base ones in Fig. 14 was due to the presence of undissolved intermetallic compounds. Among the alloys as shown in Fig. 14 (a), Ca containing alloy was the only one showed precipitation hardening effect. This can be explained in terms of the microstructure. Because of the resolution limitation of the optical microscope, microstructure illustrated in Fig. 15 (A1- A4) and Fig. 15 (B1- B4) is similar. However, TEM micrograph, as shown in Fig. 16 from reference [26], along the [10-10] axis very fine plate-like precipitates formed lying on the basal plane (0001) of Mg. These precipitates are believed to be responsible for the hardness increase.

Conversely, the Mg-9.0wt.%Al based alloys showed solid solution strengthening effect. However, the peak aged hardness for all samples was reached at much longer ageing time close to 24 hours. Moreover, Mg-9.0wt.%Al-0.5wt.%Ca sample showed almost the same behaviour as that of the base alloy. By looking at the as solution treated micrographs in Fig. 15 (A5- A8) and their corresponding aged ones in Fig. 15 (B5-B7), it will be noted that the Mg_{17}Al_{12} is the only phase has been precipitated during ageing. Hence, the precipitation hardness behaviour in Fig. 14 (b) can be
regarded as the contribution from the precipitation hardening of Mg$_{17}$Al$_{12}$ phase only. Unexpected behaviour of Mg-9.0wt.%Al-0.5wt.%Ca sample might be regarded to the low Ca concentration as the only sample showed precipitation hardening in Fig. 14 (a) had an addition level of 5.0 wt.% Ca.

![Fig. 15: Typical metallographs for as-solution treated samples (A) and their corresponding 24 hours aged ones in (B). (A1-A4 and B1-B4) Mg-3.0wt.%Al based alloys with addition of (A1 and B1) base alloy, (A2 and B2) 3.0wt.%Si, (A3 and B3) 3.0wt.%Cu and (A4 and B4) 5.0wt.% Ca. (A5-A8 and B5-B8) Mg9.0wt.%Al based alloys with addition of (A5 and B5) base alloy, (A6 and B6) 3.0wt.%Si, (A7 and B7) 3.0wt.%Cu and (A8 and B8) 0.5 wt.% Ca]
Fig. 16: Bright field TEM micrograph for Mg-Al-Ca ternary alloy along the [10-10] axis and corresponding spot patterns [26].

5. Conclusions:

(1) Addition of Si or Sn into the Mg-3wt%Al nd Mg-9wt%Al alloys led to grain coarsening in the as-cast alloys resulted from the poisoning effect with increasing the addition levels of the solutes.
(2) Cu addition to Mg-Al base alloys led to slight grain refinement.
(3) Grain coarsening was also obtained with Ca addition to Mg-Al based alloys due to the reaction between Ca and Al, which lowered the actual content of Al.
(4) Due to limited solubility of Ti in Mg, no noticeable changes in grain size and hardness were observed when Ti was added into the Mg-Al based alloys.
(5) Addition of Mn changed the grains morphology from equiaxed to columnar at 0.5wt.% and 1.5wt.% addition levels in Mg-3.0wt.%Al and Mg-9.0wt.%Al alloys respectively.
(6) Formation of intermetallic compounds played a major role in increasing alloys hardness in Si, Sn, Ca and Cu containing alloys while.
(7) The Mg-3.0wt%Al-5.0wt.%Ca alloy showed precipitation hardening effect even though no obvious change in the microstructure could be found.
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References:


Chapter 7: Outcomes, Conclusions and Future Work

7.1. Outcomes and Conclusions

In the past three years, work done in this PhD has been directed towards fulfilling these three objectives; a) developing an effective new grain refiner for Mg alloys; b) studying the effects of the new grain refiner on the mechanical properties of Mg alloys; c) investigating the effects of solutes and potent nucleants under different casting conditions on Mg alloys grains in order to help understanding the mechanism of grain refinement. Over the course of this PhD, several articles have been published which together significantly contribute in understanding the grain refinement mechanism in Mg alloys. Outcomes of the PhD project are summarized as follows:

1. The latest findings in the literature on grain refinement of Mg alloys, including the effects of widely used solutes and inoculants have been summarized. In addition, the major theoretical considerations and models commonly used to understand the grain refinement mechanism have been combined and briefly explained. Also, the Q-values of some binary alloys that have never been reported before were calculated and listed. The work forms a strong database for literature especially for developing new grain refiners for Mg alloys.

2. Using the E2EM model, a new grain refiner (CaO) has been developed for cast Mg alloys. It is found that addition of CaO into pure Mg, Mg-Zn or Mg-Ca alloys leads to significant grain refinement. CaO nucleating particles were found at the centres of Mg grains. In addition to the role of CaO potent nucleants, decomposition of some CaO particles introduces Ca solute in the melt which contribute in enhancing the grain refining efficiency. Compared with Ca solute, CaO seem to have better grain refining efficiency for cast pure Mg.

3. On the other hand, grain coarsening was obtained with CaO addition into Mg-Al based alloys. Thermodynamic calculations show that, during casting, Ca has more affinity to react with Al solute over Mg to form Al$_2$Ca intermetallic compounds leading to the loss of solutes effects in the melt.

4. Effect of CaO grain refinement on mechanical properties of cast Mg alloys was investigated. At the same addition levels, effects of CaO and Ca solute on the mechanical properties were very close. However, higher grain refinement strengthening component is found in CaO containing alloys than that of Mg-Ca.
5. Through studying the effect of cooling rate on various binary Mg alloys, it was found that higher cooling rate does not always lead to grain refinement during solidification. Grain coarsening can be obtained in some Mg alloys when the cooling rate exceeds a critical value. Using the interdependence theory it is found that at very high cooling rate the constitutionally undercooled zone ahead of the S/L interface lies within the nucleation free zone. Hence, grain growth is more likely to occur than nucleation of new grains.

6. In Mg-Al based alloys; addition of Si, Sn, Cu or Ca as a ternary element leads to higher hardness through the formation of hard intermetallic compounds. Due to the very limited solubility of Ti in Mg, addition of Ti solute into Mg melt is rather challenging. It has been experimentally proven that addition of Ti into Mg-Al alloys has only a minor effect on grains size and almost no effect on hardness. Increasing the addition levels of Mn to Mg-Al based alloys leads to grains structure transformation from equiaxed to columnar. Also, Mn is the only solute found to be decreasing hardness values of Mg-Al based alloys with increasing its addition level. After aging, it was found that from all the ternary elements studied, only Ca showed precipitation hardening effect.

7. Based on the results obtained in the current work, a number of considerations need to be taken into account in order to develop an effective grain refiner for Mg alloys:

a) Due to the high chemical activity of Mg, the chemical reactions before solidifications must be taken into account.

b) Crystallographic matching is a highly useful approach in predicting the potency of inoculants and particularly in-situ forming particles.

c) Best grain refining efficiency can only be obtained through combining the effect of solutes with presence of potent nucleating particles in the melt.
2.7 Future work

Even though the results in this PhD have made some achievements in the area of grain refinement of Mg alloys, the research also arises some new important issues that remain unsolved and need more research to understand/solve them. They are listed as follows:

1. Regarding the grain refinement behaviour in binary Mg alloys, it has been found that even though Al has a considerably low Q-value with Mg, it has a much higher refining efficiency on Mg than many other solutes. Hence, it is important to perform an in-depth investigation on the effects of Al solute on Mg to fully understand whether any in-situ particles are formed during solidification that might act as potent nucleating sites and promote heterogeneous nucleation of the grains.

2. Following the effect of cooling rate on grain refinement of Mg alloys, it is important to fully understand the concept of critical cooling through carrying out a number of experiments and find the critical cooling rate value for each alloy. Such study will provide a major breakthrough in casting alloys design particularly for castings techniques such as HPDC which use very high cooling rate.

3. It would be interesting to comprehensively study the effects of Mn on Mg-Al alloys because according to the phase diagram, intermetallic compounds should form which in return lead to increasing hardness but in the current study, hardness was found decreasing with increasing Mn addition levels and microstructure micrographs showed no presence of intermetallics.
References


