INVESTIGATION OF THE EFFECT OF RARE EARTH ADDITIVES ON SOLIDIFICATION OF AS-CAST ZREI MAGNESIUM ALLOY

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This thesis is dedicated to my mother, father, and my family.
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ABSTRACT

The thesis project investigates the effect of alloying elements Pr, Y and Er addition on the solidification characteristics, microstructure and mechanical properties of as-cast ZRE1 magnesium alloy. Automotive and aerospace industries shall witness the advancement to the next generation if magnesium alloys becomes an integral part of their manufacturing unit primarily because of its light weight. The main limitation which hinders the progress in this direction is the inferior mechanical properties of Mg alloys. Rare earth elements were used as alloying elements for improving the mechanical properties and to introduce a new Mg-RE alloy with modified structure and strength. In addition, this study demonstrates the addition of RE at specific amounts which could be considered as main alloy elements that may lead to extent limitation of RE application. 0.25, 0.5, 0.75, 1, 1.25 and 1.75 wt.% of Pr, Y and Er were added separately to ZRE1 magnesium alloy. Thermal analysis was examined using CA-CCA. XRD, OM and FESEM/EDS were used to investigate the microstructure of alloys, and the mechanical properties investigated include tensile and hardness tests. The results revealed that as Pr level reached 1.25 wt.%, the solidification time was reduced to 52 s, the grain size decreased by 12%. Addition of 0.5 wt. % of Er caused a decrease in the solidification time of about 20% which led to a decrease grain size of about 16%. Furthermore, solidification time decreased of about 23 s which led to grain size reduction by 24% as addition of 1 wt.% Y. UTS and YS were improved by 10% and 11% respectively through addition of 1.25 wt.% of Pr. Moreover, UTS increased by 17% and 8% for YS at 1.25 wt.% of Y. Addition of 0.25 wt. % of Er led to increase UTS and YS by 15% and 7% respectively. In addition, the hardness value of base alloy was also recovered. The additives had a significant effect on the solidification time, leading to the refinement of the microstructure, and improved the mechanical properties, thus the ZRE1 magnesium alloy was developed. Lastly, casting and machining parameters of the developed alloys are recommended to be examined.
ABSTRAK

Tesis ini mengkaji kesan penambahan unsur pancalogam Pr, Y dan Er ke atas ciriciri pemelajaran, mikrostruktur dan sifat mekanikal pancalogam magnesium ZRE1. Penggunaan pancalogam magnesium yang lebih ringan dalam proses pembuatan dalam industri otomotif dan aeroangkasa akan memperlihatkan peningkatan ke arah satu era baru dalam kedua-dua industri tersebut. Walau bagaimanapun, sifat mekanikal pancalogam magnesium yang berprestasi rendah boleh menghalang peningkatan tersebut. Dalam kajian ini, unsur nadir bumi (RE) digunakan untuk mengubah struktur dan kekuatan bagi mempertingkatkan sifat mekanikal pancalogam magnesium, dan seterusnya menghasilkan pancalogam Mg-RE. Kajian ini juga menguji had penambahan RE dengan jumlah tertentu. Sejumlah 0.25, 0.5, 0.75, 1, 1.25 dan 1.75 wt.% Pr, Y dan Er ditambah ke atas pancalogam magnesium ZRE1 secara bersaringan. Analisis terma dilaksanakan menggunakan CA-CCA. XRD, OM manakala FESEM/EDS digunakan untuk mengkaji mikrostruktur pancalogam. Sifat mekanikal yang dikaji ialah ujian ketegangan dan kekerasan. Dapatkan kajian menunjukkan jangka masa pemelajaran dikurangkan ke 52s dan saiz serpihan/bijirin mengecil 12% apabila tahap Pr mencapai 1.25 wt%. Penambahan Er sebanyak 0.5 wt.% menyebabkan jangka masa pemelajaran berkurangan 20% dan ini menyebabkan saiz serpihan mengecil 16%. Di samping itu, jangka masa pemelajaran dikurangkan 23s menyebabkan saiz serpihan mengecil 24% dengan penambahan Y sebanyak 1 wt.. Terdapat peningkatan UTS dan YS, masing-masing 10% dan 11% dengan penambahan Pr sebanyak 1,25 wt.. UTS juga meningkat 17% manakala prestasi YS meningkat 8% dengan penambahan Y sebanyak 1.25wt%. Penambahan Er sebanyak 0.24 wt% menyebabkan peningkatan UTS dan YS, masing-masing 15% dan 7%. Selain itu, kajian ini juga dapat mengkaji tahap kekerasan pancalogam. Penambahan unsur nadir bumi memberikan impak yang signifikan terhadap jangka masa pemelajaran, yang menyebabkan penambahan mikrostruktur dan sifat mekanikal, yang menghasilkan pancalogam magnesium ZRE1. Akhir sekali, satu kajian susulan perlu dilaksanakan untuk mengkaji parameter pengacuan dan pemesinan pancalogam yang telah dihasilkan.
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<tr>
<td>$T_G$</td>
<td>Growth temperature</td>
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<tr>
<td>$T_s$</td>
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<tr>
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<tr>
<td>tDCP</td>
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LIST OF ABBREVIATION

CA-CCA  -  Computer Aided Cooling Curves Analysis
G-B Zone  -  A Guinier–Preston zone
ASTM   -  American Society Testing Materials
BCC   -  Body Center Cubic
FCC   -  Face Center Cubic
HCP   -  Hexagonal Close Packed
EDS   -  Energy-Dispersive X-ray Spectroscopy
FESEM -  Field-Emission Scanning Electron Microscope
UTS   -  Ultimate Tensile Strength
SY    -  Yield Strength
XRD   -  X-Ray Diffraction
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CHAPTER 1

INTRODUCTION

1.1 Research Background

Magnesium and magnesium alloys are used in a wide variety of structural and nonstructural applications due to its light-weight, which is the lowest density of all structural metals and have high strength-to-weight ratios (tensile strength/density), comparable to those of other structural metals. Magnesium has relatively good electrical conductivity and thermal conductivity values, and also has a very high damping capacity, that is the ability to absorb elastic vibrations [1]. Protecting the atmosphere and reduction of CO₂ traffic emissions grew in importance in the social discussion. Reduction in fuel consumption for motor vehicles therefore had a significant influence on CO₂ emissions. Reduction in vehicle mass leads to reduction in fuel consumption. Magnesium alloys, with their low density of approximately 1.8 g/cm³, are considered seriously contenders for lightweight vehicle manufacture. A reduction of 25% weight was achieved with the procedure of a gearbox housing made of AZ91 magnesium alloy, compared to an existential lightweight aluminium design [2, 3].

Magnesium alloys are used in structural applications mostly as die casting. These applications include automotive, industrial, materials handling, commercial, and aerospace equipment. The automotive applications include instrument panel support beams, brake and clutch pedal brackets, air intake grills, steering column support brackets, steering wheels, seat back frames and seat bottoms, and battery cases for electric vehicles. In industrial machinery such as textile and printing
machines, magnesium alloys are used for parts that operate at high speeds and thus must be lightweight to minimize inertial forces. Materials-handling equipment includes dockboards, grain shovels, and gravity conveyors. Commercial applications include hand-held tools, computer housings, and mobile-phone cases. Magnesium alloys are valuable for aerospace applications as well which include main transmission housings for helicopters and gearboxes and gearbox housings for commercial and military aircraft [4, 5]. Magnesium is also used in nonstructural application, where it is used as alloying element with aluminum. Magnesium is also used as an oxygen scavenger and desulfurizer in the manufacture of nickel and copper alloys; as a desulfurizer in the iron and steel industry; and as a reducing agent in the production of beryllium, titanium, zirconium, hafnium, and uranium. Another important nonstructural use of magnesium is in the Grignard reaction in organic chemistry, where magnesium is used in photoengraving [6]. Figure 1.1 shows scheme of the developments in magnesium alloys.

![Development in Mg alloys](image)

Figure 1.1: Development in Mg alloys [6]

Mg alloys can be divided into cast magnesium alloys and wrought Mg alloys. The main commercial of Mg alloys include the AZ series (Mg-Al-Zn), AM series
(Mg-Al-Mn), AE series (Mg-Al-RE), EZ series (Mg-RE-Zn), ZK series (Mg-Zn-Zr), and WE series (Mg-RE-Zr). Statistically, more than 90% of the Mg alloy structural components are produced by casting process [7-9].

Rare Earths elements (RE) are added to magnesium alloys to improve the high temperature strength and creep resistance [4]. They are usually added as mischmetal (MM) or didymium (Dm). Mischmetal is a natural mixture of the RE containing about 50 wt% cerium (Ce), with the remainder being principally comprising lanthanum (La) and neodymium (Nd), and didymium which is a natural mixture of approximately 85% neodymium (Nd) and 15% praseodymium (Pr) [10, 11]. At present, the RE elements added into Mg alloy are roughly divided into two categories. First category is the elements with small solid solubility such as Ce, and Pr element. Second category is the elements with large solid solubility such as Y, Nd, La element etc [12]. Many RE elements by preformed alloy forming are added to the magnesium alloy. RE elements, such as Gd, Er and Y, are added to the magnesium result in changes to mechanical properties such as increased tensile strength, creep resistance, thermal stability, and corrosion resistance [13, 14].

Magnesium-rare earth-zinc-zirconium alloys show good casting characteristics because the presence of the rare earth elements promotes formation of relatively low melting point eutectics that improve fluidity and tend to prevent microporosity. The properties of Mg-RE alloys are enhanced by adding zirconium to refine grain size and further increase in strength occurs if zinc is present as well [15]. Rare-earth containing magnesium based alloys such as RZ5 (ZE41) designed by Magnesium Elektron is a magnesium casting alloy of medium strength which is ideal for high integrity casting operating at ambient temperatures. ZE41 (Mg - 2Zn -1.3RE - 0.6Zr) develops moderate strength when given a T5 ageing treatment which is maintained up to 150 °C [16].

Higher creep strength at temperatures up to 250 °C have been achieved in the Elektron ZRE1 magnesium alloy. Elektron ZRE1 is a magnesium based casting alloy fabricated by Magnesium Elektron Ltd, and containing zinc, rare earth and zirconium. The alloy exhibits excellent casting characteristics with components being both pressure tight and weldable, and it is completely free from micro-porosity and suitable for applications requiring pressure tightness [17]. Elektron ZRE1 is used in aero engine components where improved creep resistance is required. In the aero-engine industry, magnesium alloys are being used successfully in both civil and
military aircrafts. Civil applications include intermediate casings for engines and 
gearboxes & also in military aircraft, including the F16, Tornado and Eurofighter 
Typhoon, which capitalize on the lightweight characteristics of Mg alloys for 
transmission casings [18, 19].

RE elements are normally present as solutes in α-Mg matrix or as RE-
containing phases both of which might provide strengthening effects [20]. 
Praseodymium (Pr) is a rare earth metal with a low solid solubility in magnesium 
(1.7 wt.%), and used for alloying agent with magnesium to create high-strength 
metals that are used in aircraft engines [21]. Yttrium (Y) has a relatively high solid 
solubility in Mg (12.4 wt%), and enhances strength and creep performance when 
combined with other RE metals [22]. The maximum solubility of erbium (Er) in 
magnesium at 540 °C is 32.7 wt%, but decreases to 18.5 wt% at 300 °C, which 
means that Er might bring about a great effect of dissolution and precipitation 
hardening. Therefore Er is considered to be of great potential to be used as a modifier 
of Mg alloys [23].

Thermal analysis is a very useful tool to investigate the solidification 
characteristics of alloys. The solidification characteristics of metals and alloys can be 
investigated through various thermal analysis techniques. Computer-aided cooling 
curve analysis (CA-CCA) is much more suitable for industrial applications compared 
to other methods, due to its ease of use and low cost. (CA-CCA) has also been 
successfully applied in investigations of the solidification sequences of Mg alloys in 
recent years. Many researchers have used thermal analysis to investigate the 
influence of additives and processing steps on the parameters of the cooling curve of 
magnesium alloys [24-26].

The ability of Pr, Y and Er additions to improve strength and hardness of 
ZRE1 magnesium alloy will be approved. However, given the different 
characteristics of the individual RE elements, obtaining a high strength and hardness 
is challenging, appears to be a substantial change in the microstructure. Another 
challenge with single RE additions which is for each of the RE elements there is an 
increase in strength and hardness with different mechanism. So, micro-alloying with 
addition of single Pr, Y and Er could strengthening ZRE1 alloy by different ways, 
and that makes elicitation of the strengthening mechanisms more complicated.
1.2 Problem Statement

Lightweight magnesium (Mg) alloys are being increasingly used for applications, such as the automotive industry, where weight savings are critical. However, the limited mechanical properties of Mg alloys has retarded their applications, which makes it unsuitable for many of the components [27]. One of the Mg–Zn–RE–Zr alloys earlier available is Elektron ZRE1, whose founding strength and hardness are poor [28]. The strength of Mg alloys can be enhanced by adding proper amounts of certain alloying elements [29, 30]. In order to develop new alloys to achieve higher strength to compete with currently used metal alloys, it is important to understand the effects of alloying elements on the microstructure, mechanical properties. The addition of single rare earth to Mg-Zn-Zr alloy results in great improvement in mechanical properties [30]. In the case of Pr, Y and Er as alloying elements can be used for solid solution strengthening, grain refinement and grain boundary reinforcement which are useful when the strength and hardness to be improved [31-34]. It has been reported that Pr, Y and Er elements can form several intermetallic secondary phases in Mg–Zn–Zr alloy, and has a favourable effects on the mechanical properties [32, 33, 35]. The formation of hard secondary phase contributes to the increasing of strength, where the mechanical properties of Mg alloys are strongly influenced by volume fraction and distribution of intermetallic phases [36, 37].

Unfortunately, not all the secondary phases have positive effects on the mechanical properties. So, it is essential to reveal the phase constituent for the Mg-Zn-RE-Zr system alloys. Generally, the I-phase, Z-phase and the W-phase usually form based on the chemical compositions of the Mg–Zn–RE–Zr alloys. As reported, the I-phase and Z-phase have good properties, such as high hardness and low surface energy, which are great beneficial to improve the tensile strength. Otherwise, the W-phase has weak bonding with Mg matrix, and was easily cracked during the tensile process, which is harmful to the mechanical properties. So, the W-phase is generally not considered as a very effective strengthening phase [38-44].

In order to overcome the above mentioned problems encountered in Mg-Zn-RE-Zr alloys, the addition of proper amount of single rare earth into ZRE1 magnesium alloy, this is the most promising method to improve the mechanical properties. The developed testing methodology will be valuable for future alloying studies on Mg-RE alloys systems. Overall, the insights gained from this dissertation
will have a broad impact on understanding the strengthening behaviour and microstructural evolution of RE-containing Mg alloys, and such insights can serve as guidance for the development of new alloys and processes.

1.3 Research Objectives

This thesis presents the influence of rare earth additives, praseodymium (Pr), yttrium (Y), and erbium (Er) on solidification characteristics of as-cast ZRE1 magnesium alloy. The specific objectives of the research include the followings:

(i) Develop a new Mg-RE alloy with modified structure and strength. This development will enable to expand the use of Mg-RE alloys applications, and will be introduce to replace competitive lightweight materials.

(ii) Control the microstructure obtained from different solidification characteristics, and thus attain desired properties. Understanding of the microstructure evolution and the resulting properties is of paramount importance.

(iii) Improve the mechanical properties of ZRE1 magnesium alloy by the addition of small concentrations of rare earth elements separately. With an explanation of the impact of Pr, Y and Er on the strengthening mechanism of the alloy.

(iv) Analyse the effect of additives on the solidification behavior, microstructure and strengthening mechanisms of ZRE1 alloy at various states gives us a clear picture showing the relationships of alloy composition, microstructure and mechanical properties improvement. This result enables the development of high strength Mg alloys.

1.4 Scope of Study

(i) RE additions were used to assess the degree of additives for refinement of microstructure and intermetallic phases formation, which was carried out by computer aided cooling curve thermal analysis (CA-CCTA) technique. This technique can predict the formed phases and the microstructure characteristics by obtaining the solidification parameters from the alloy cooling curves.
(ii) Find the proper way to develop the base alloy by modify the microstructure and identify the mechanism of strength, where the understanding of how the alloying elements affect these mechanisms is the key to improve a new Mg-RE alloy.

(iii) Develop a new method to improve mechanical properties (tensile and hardness) by choosing the proper amount of additives to form hard intermetallic phases and refine the microstructure.

1.5 Organization of the Thesis

This dissertation comprises five chapters. A research background, problem statement, research objective, scope of study and organization of the thesis are provided in Chapter 1. The second chapter provides the literature review. A review of the literature relevant to the Mg and its alloys, Mg-Zn-RE alloys, ZRE1 magnesium Alloy, effect of RE elements on Mg-Zn alloys, and solidification of cast Mg-Zn Alloys. The experimental procedure is presented in Chapter 3, including the experimental information of investigated alloy and alloy preparation. Following this, the testing steps, which include thermal analysis, microstructure and mechanical properties. The results and discussion are presented in chapter 4, which discuss and review the data recorded from the experiment conducted in chapter three. Chapters 4 reviews the data recorded from the thermal analysis, microstructure observations and mechanical properties of the base alloy and alloys treated with Pr, Y and Er. Chapter 5 summarises the conclusions of this research, contribution of study and suggest areas for future research.
CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter focuses on literature reviews of magnesium-rare earth casting alloys and their properties in relation to a number of metallurgical parameters. Rare earth elements addition will be discussed regarding their effects on the solidification, microstructure and mechanical properties of Mg alloys. Solidification behavior and grain refinement in Mg-Zn-RR alloys will also be covered.

2.2 Magnesium and Its Alloys

In 1808, magnesium was discovered and isolated by Sir Humphrey, it took about 100 years before a real demand for magnesium developed. Since the second world war, when there had been an increase in the use of magnesium in structural uses (about 228,000 tons in 1944), at most for aircraft, it took more than another 40 years to reach the same level in 1992. Since 1993 there has been renewed interest in using magnesium alloys in automobile and other household and sport applications [4, 45].

The beginning of 2000s brought the development of casting alloys with high creep resistance and low-to-moderate cost, for use in powertrain applications. Magnesium – aluminum – strontium alloy, developed by Noranda, was used in BMW engine blocks from 2004 to 2009 [46]. These activities were not sufficient to develop a steady Mg supplier base, either in North America or in Europe, and, despite the low cost production of Mg in China in the latter part of the decade (2000-
The new decade from 2010 onward is seeing interest in Mg wrought alloys for use in the automotive body (closures, front-end structure, roof pillars) [46]. Extrusion and sheet alloys are currently being developed to improve formability in wrought magnesium. Interestingly, these alloys, like creep-resistant casting alloys, are also based on RE and Sr additions to magnesium. Magnesium and its alloys are used in a wide variety of structural and nonstructural applications [48]. Structural applications include automotive, industrial, materials-handling, commercial, and aerospace equipment. The automotive applications include clutch and brake pedal support brackets, steering column lock housings, and manual transmission housings [49]. Cast or forged magnesium wheels have been used in many high-priced racing-cars or high-performance roadsters, including GM’s Corvette. In industrial machinery, such as textile and printing machines, magnesium alloys are used for parts that operate at high speeds and thus must be lightweight to minimize inertial forces. Materials-handling equipment includes dockboards, grain shovels, and gravity conveyors. Commercial applications include hand-held tools, luggage, computer housings, and ladders. Magnesium alloys are valuable for aerospace applications because they are light-weight and exhibit good strength and stiffness at both room and elevated temperatures [50]. Magnesium is also employed in various nonstructural applications, where it is used as an alloying element in alloys of aluminum, zinc, lead, and other nonferrous metals. Aluminum and zinc are relatively soluble in solid magnesium, but their solubilities decrease at low temperatures. The solubility of aluminum is 12.7% by weight at 437 °C and 3.0% at 93 °C, solubility of zinc is 6.2% at 340 °C and 2.8% at 204 °C, Solubilities of manganese, zirconium, and cerium are less than 1.0% by weight at 482 °C. At the eutectic temperature, 4.5% thorium is soluble in magnesium [1, 6]. Magnesium is classified as an alkaline earth metal. It is found in Group 3 of the periodic table. It thus has a similar electronic structure to Be, Ca, Sr, Ba and Rd. Atomic number 12, atomic weight 24.3050, atomic diameter 0.320 nm and atomic volume 14.0 cm³/mol [51]. The crystal structure of magnesium is hexagonal close packed, and its lattice parameters estimated at room temperature are: a = 0.32092 nm, c = 0.52105 nm and the c/a ratio is 1.6236 which is close to the ideal value of 1.633 [1]. Therefore, magnesium considered as perfectly closed packed. The density of magnesium at 20°C is 1.738 g/cm³ and at the melting point of 650 °C this value reduced to 1.65 g/cm³, also on melting there is an expansion in volume of 4.2 % [52]. There are six sources of raw
materials for the production of magnesium: magnesite, dolomite, bischofite, carnallite, serpentine and sea water [1].

Mechanical properties of pure magnesium are comparatively poor. Ultimate tensile strength it is about 90 MPa for sand cast magnesium and yield strength 21 MPa, hardness 30 HB [6]. To enhance such mechanical properties, it is therefore necessary to add some alloying elements which can modify certain characteristics of the pure material by solid solution strengthening, precipitation hardening or grain size refinement [53].

2.2.1 Magnesium Alloys Designation System

There is no international system for designating magnesium alloys, although in 1948 there has been a trend toward adopting the naming method used by ASTM for magnesium alloys [8, 47]. The first part consists of code letters indicating the two principal alloying elements, listed in order of decreasing alloying content. The second part consists of the weight percentages of these two elements, rounded off to the nearest whole number and listed in the same order as the code letters. The third part consists of an assigned letter (beginning with “A”) to distinguish between alloys having the same nominal designation, or an “X” to indicate that the alloy is still experimental. The third part consists of a code system for the temper of magnesium (and other) alloys. This consists of a letter plus one or more digits. The temper designation follows the alloy designation and is separated from it by a hyphen. For example, AZ91E-T6, the first part of the designation, AZ, signifies that aluminum and zinc are the two principal alloying elements. The second part of the designation, 91, gives the rounded-off percentages of aluminum and zinc (9 and 1, respectively). The third part, E, indicates that this is the fifth alloy standardized with 9 % Al and 1 % Zn as the principal alloying additions. The fourth part, T6, denotes that the alloy is solution treated and artificially aged [48, 54].

The primary product forms for magnesium alloys are pressure die castings, which make up 28.5% of magnesium consumption. Magnesium alloys are also produced by sand casting, permanent mold casting, investment casting, and thixotropic molding (semisolid injection molding). Wrought products, which account for only 1% of magnesium consumption, are available as forgings, extruded bars and shapes, and sheet and plate [6, 55].
For engineering applications, magnesium must be alloyed with other metals. The vast majority of the alloy systems currently being commercially produced contain aluminum, manganese, zinc, zirconium, rare earths, and silver in order to obtain the strong, light weight alloys needed for structural uses [4].

Although thorium-containing alloys have found applications in missiles and spacecraft, they have lost favor because of environmental considerations and are generally considered obsolete. All of the alloy systems listed previously can be generally grouped into those that contain aluminum as an alloying element and those that do not. Because most alloys that do not contain aluminum as an alloying element contain zirconium additions to refine the grain structure (magnesium manganese alloys are the main exception), commercial magnesium alloy systems can be alternatively grouped as zirconium-free and zirconium containing. The specific alloys can also be classified as to product from: cast, or wrought [56, 57].

The Mg-Al system is the basis of the most widely used alloys. The most commonly used magnesium die casting alloy is AZ91D, it is exhibits good mechanical and physical properties in combination with excellent castability and saltwater corrosion resistance [58]. Die castings are used in the as-cast condition. Normally smaller components of magnesium are cast by die casting, sand mould, permanent mould and low-pressure casting, etc. The choice of a particular casting method depends on many factors, e.g., the number of castings required, the properties required, the dimensions and shape of the part and the castability of the alloy [46]. Die cast alloy AS41A has creep strength much superior to that of the AZ91D or AM60B alloys at temperatures up to 175°C, it also has good elongation, yield strength, and tensile strength. The AS41A alloys was used in crankcases of air-cooled automotive engines [59]. A high-purity version of AS41A, which exhibits excellent saltwater corrosion resistance, is being introduced as AS41XB. The AS21 alloy exhibits even better creep strength than AS41A. However, AS21 has lower room-temperature tensile and yield strengths, and it is somewhat more difficult to cast [60]. Magnesium forms solid solutions with a number of rare earths and show simple eutectics. The alloys have good casting characteristics and the age hardening response is also good. The alloys also have good creep properties. The Mg-RE (EZ) alloys can be grain refined using Zr. Although the role of Zn is uncertain, it adds strength. Typical alloys are ZR5 (ZE41) (Mg-4.2Zn-1.2Ce-0.6Zr) and ZRE1 (EZ33) (Mg-3RE-2.5Zn-0.6Zr). Sand and Permanent Mold Casting Alloys [61].
2.2.2 Influence of Alloying Element Additions on Magnesium

Magnesium alloys can be produced by melting magnesium pigs and then adding the alloying metals. Most foundries, purchase prealloyed ingot, which is subsequently charged into the melting furnace with a proportion of process scrap. Magnesium exhibits significant property improvement via alloying. Magnesium alloy research in the past two decades has further shown that magnesium can be designed to improve mechanical properties, corrosion resistance and formability [62]. Usually, alloying metals and master alloys are added into the melt, which is held at about 700 °C, as sawed pieces of ingot. When alloying with zirconium, a technique involving either manual or mechanical stirring, followed by a settling procedure to allow acid-insoluble zirconium complexes to settle, is required to produce the required degree of supersaturation of the melt with zirconium [6].

Rare earth metals are added to magnesium alloys either as mischmetal (MM) or as didymium (Dm) [63]. Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium, with the remainder being principally comprised of lanthanum and neodymium, didymium is a natural mixture of approximately 85% neodymium and 15% praseodymium [4]. Additions of the rare earths increase the strength of magnesium alloys at elevated temperatures. They also reduce weld cracking and porosity in casting because they narrow the freezing range of the alloys [64].

Magnesium forms solid solutions with a number of RE elements. The addition of cheaper mischmetal based on cerium or neodymium to magnesium gives good casting characteristics and mechanical properties [6]. These properties are improved by adding Zr to refine the grain size, and further increases in strength occur if zinc is added as well, such as ZRE1 (Mg-3RE-2.5Zn-0.6Zr) which retains strength and creep resistance at temperatures up to 250 °C. Recently, Mg-Y age-hardenable alloy systems have been developed to use the benefit of high solid solubility of yttrium in magnesium. A series of Mg-Y-Nd-Zr alloys have been produced that provide high strength at ambient temperature and good creep resistance up to 300 °C temperature [65]. Maximum strength combined with an adequate level of ductility is found to occur in an alloy containing approximately 6% Y and 2% Nd and the
commercially available alloy in this category is WE54 (Mg-5.25Y-3.5RE-0.45Zr) [66].

Zinc is next to aluminium in effectiveness as an alloying ingredient in magnesium. Zinc is often used in combination with aluminium to produce improvement in room-temperature strength; however, it increases hot shortness when added in amounts greater than 1 wt% in magnesium alloys containing 7 to 10 wt% aluminium [67]. Zinc is also used in combination with zirconium, rare earths, or thorium to produce precipitation-hardenable magnesium alloys with good strength. Zinc also helps overcome the harmful corrosive effect of iron and nickel impurities that might be present in the magnesium alloy [68].

Zirconium has a powerful grain-refining effect on magnesium alloys [69]. It is thought that because the lattice parameters of α-zirconium (a = 0.323 nm, c = 0.514 nm) are very close to those of magnesium (a = 0.320 nm, c = 0.520 nm), zirconium-rich solid particles produced early in the freezing of the melt may provide sites for the heterogeneous nucleation of magnesium grains during solidification [70]. Zirconium is added to alloys containing zinc, rare earths, thorium, or a combination of these elements, where it serves as a grain refiner (up to its limit of solid solubility). However, it cannot be used in alloys containing aluminium or manganese because it forms stable compounds with these elements and is thus removed from solid solution [21]. It also forms stable compounds with any iron, silicon, carbon, nitrogen, oxygen, and (mainly) hydrogen present in the melt [71].

In general, the most effective way to improve the mechanical and microstructure properties of magnesium is by alloying with additional elements. The improvement of mechanical properties can be influenced directly by increasing the content of solute element in solid solution.

2.3 Mg-Zn alloys

Zinc is an important alloying element but rarely serves as the major alloying element (ZK, ZH, ZM, ZC and ZE series of alloys) [72]. It has a very good solid solubility in magnesium. The Mg-Zn binary phase diagram given in Figure 2.1 shows that the maximum solubility of Zn in Mg at 345°C (eutectic temperature) is around 6.2%. The solid solubility of zinc in magnesium at room temperature is around 2%. So the excess zinc forms Mg_{51}Zn_{20} intermetallic with Mg. This phase is hard and brittle and
hence acts as a strengthening element at room temperature [73]. Zinc also improves the fluidity of the alloy, but a higher amount of Zn added to Mg-Al alloys can lead to hot cracking problems. The selection of zinc content into magnesium aluminum alloy is based on the content of wt% of Zn and Al in the castable region [6]. The presence of zinc decides the type of eutectic (completely or partially divorced) during the final stage of solidification. It is further reported that the addition of zinc reduces the ductility of the alloy [16].

![Phase diagram of Mg-Zn system](image)

**Figure 2.1: Phase diagram of Mg-Zn system [51]**

Zinc causes more solid solution strengthening than an equal atomic per cent of aluminum but its solubility is much less [6]. Mg-Zn alloys also respond to age hardening, the ageing process is complex and may involve four stages. The GP zones (Guinier–Preston) solves for the alloy Mg-5.5Zn lies between 70 and 80 °C, and preageing below this solves before ageing at a higher temperature (e.g. 150 °C) refines the size and dispersion of rods of the coherent phase MgZn₂ that form the GP zones. Maximum hardening is associated with the presence of this coherent phase [74]. However, binary Mg-Zn alloys are not amenable to grain refining by superheating or inoculation, and are prone to microporosity. Consequently, they are not used for commercial castings. Minor additions may modify precipitation in Mg-
Zn alloys. Examples are the elements calcium and strontium which accelerate the rate of ageing but delay overageing, refine the sizes, and increase the number densities of precipitates that form [75].

2.3.1 Magnesium-zinc-rare earth alloys

Mg-Zn based alloys have been shown to have better high temperature performance than equivalent Mg-Al alloys, particularly where stable precipitates can be introduced. Unfortunately, increasing Zn content leads to a deterioration in corrosion resistance, even for high purity alloys, so that Zn additions are restricted to less than 2wt%. To achieve significant improvement in properties of Mg-Zn alloys, rare earth elements have been added [76, 77].

A UK based company (Magnesium Elektron) developed an alloy designated MEZ (Mg-2.5RE-0.5Zn-0.35Mn) that has potential automotive applications such as gear boxes and oil pans [6]. This alloy was designed for use in high pressure die castings and therefore does not require grain refining. Zinc was added to improve castability. The tensile properties are lower than for the alloy AE42, but MEZ shows superior creep resistance, especially at temperatures above 150 °C [78]. This latter behavior is attributed to the presence of a more stable compound in grain boundaries that has the general formula Mg_{12}RE and is probably Mg_{12} (La_{0.43} Ce_{0.57}) in which partial substitution of zinc for magnesium may occur [79].

Although special attention has been given to the development of magnesium alloys for high pressure die casting, this method of manufacture is not necessarily the best for casting an engine block [6]. Design variations can be accommodated more readily when using permanent mould or sand casting. Moreover, because such castings usually contain less porosity, they are amenable to heat treatment to improve their mechanical properties because there is little danger of swelling and blistering [80]. Several works are in progress to design and evaluate permanent mould and sand cast magnesium alloys for possible use in light weight engines. One such development has involved groups in Australia, Germany, Austria and England that have focused on producing a cost-effective, sand cast alloy that based on the Mg-RE system for use for the cylinder blocks and crank cases. This alloy has been designated AM-SCI, has the nominal composition Mg-2.7RE-0.5Zn, which is similar to MEZ. However a special combination of RE elements has been used to promote
creep resistance. It has a microstructure after a T6 temper that is generally similar to MEZ and has an intermetallic phase dispersed around the grain boundaries and triple points to minimize grain boundary sliding at the operating temperature of around 150 °C [6, 80].

2.3.2 Magnesium-rare earth-zinc-zirconium alloys

Mg-Zn-RE-Zr alloys have been widely used in aerospace and other applications at temperatures between 175 and 260 °C [81]. Because their high-temperature strengths exceed those of the magnesium-aluminum-zinc alloys, thinner walls can be used, and a savings in weight is possible. These alloys contain either the neodymium mischmetal or the cheaper cerium based mischmetal. An alloy designated MEZ (Mg-2.5%RE-0.35%Zr-0.3%Mn) has been developed by Magnesium Elektron with corrosion resistance similar to current high purity alloys and creep resistance superior to AE42 [82]. Capability to produce automotive castings such as gearboxes and oil pans has been demonstrated. These alloys also show good casting characteristics because the presence of the RE elements promotes formation of relatively low melting point eutectics that improve fluidity and tend to prevent microporosity. The properties of Mg-RE alloys are enhanced by adding zirconium to refine grain size and further increases in strength occur if zinc is present as well [83].

Zirconium (Zr) is a very effective grain refiner for magnesium. In addition, Zr can be used with all alloys except those containing Al, Si, Fe, Ni, Mn, Sn, Co and Sb, due to these elements will form stable high melting point compounds with Zr and cannot be present in Mg-Zr alloys [6]. Elements such as Al, Si and Mn are major alloying additions for commercial non-zirconium magnesium alloys, but cannot be used with Zr. Phase diagram of Mg-Zr is shown in Figure 2.2. The solubility of zirconium in magnesium is 3.8 wt % at the melting temperature and decreases to 0.2 wt % at room temperature [16, 84].
Melting and alloying of Mg-Zr alloys to produce alloys with satisfactory properties depends on an understanding of the mechanism of the grain refining effect of zirconium [6]. Although the precise mechanism is still the subject of investigation, there are a number of key factors which contribute to the grain refinement process. It is considered that zirconium is a good refiner because it has the same crystal structure and the lattice parameters are virtually identical [85]. It is well known that Zr addition to pure magnesium or appropriate alloys reduces the grain size by an order of magnitude or more compared to non-Zr containing alloys, with consequent beneficial effects on mechanical properties and casting characteristics [70, 81]. A fuller explanation of the mechanism needs to take account of other factors observed in the processing of Mg-Zr alloys such as the effect of other alloying elements and trace impurities and the indication that only Zr soluble in the liquid Mg alloy appear to take part in the grain refinement process. The subsequent development, by Magnesium Elektron in the UK, effective and practical means of introducing

Figure 2.2: Mg-Zr equilibrium phase diagram [51]
zirconium into magnesium eventually led to the development of new families of alloys based on combinations of elements not previously possible [81]. This development, driven by the needs of jet aircraft engines, resulted in a continuous improvement in strength and particularly elevated temperature resistance, culminating in current alloys such as WE43 (Mg-4%Y-3%RE (Rare Earth)-0.5%Zr) which have high strength and long term temperature stability at temperatures as high as 250 °C [66, 86].

One commonly used alloy is RZ5 (ZE41) (Mg4.2Zn-1.3Ce-0.6Zr) that develops moderate strength when given a T5 ageing treatment which is maintained up to 150 °C. One application has been helicopter transmission housings. Higher tensile properties combined with good creep strength at temperatures up to 250 °C have been achieved in the alloy ZRE1 (EZ33) (Mg-3RE-2.5Zn-0.6Zr) [1]. Alloy EZ33A has good strength stability when exposed to elevated temperatures. Strength stability is the ability to resist deterioration of strength from extended exposure to elevated temperatures [87]. This alloy is more difficult to cast in some designs than Mg-Al-Zn alloys. Alloy ZE41A is similar to EZ33A, but it has higher tensile and yield strengths because of its higher zinc content. Some sacrifice is made in castability and weldability in ZE41A to obtain the higher mechanical properties. When the operating temperature of an engine housing was increased from 120 to 205 °C, alloy EZ33A-T5 was successfully substituted for AZ92A-T6. The change was based on creep tests of separately cast bars of the two alloys, stress values for 0.1% creep in 1000 h [88].

2.3.3 ZRE1 Magnesium Alloy (Mg-Zn-RE-Zr)

(as mischmetal) 2.5-4.0 %, Zirconium 0.4-1.0 %, and Magnesium Balance. The alloy exhibits excellent casting and it is suitable for operating at temperature up to 250 °C [48]. Elektron ZRE1 is normally used in the T5 condition (10-6 hours at 170-200 C and air cooled) [90]. The typical uses of ZRE1 are pressure-tight sand and permanent mold castings relatively free from microporosity, used in T5 condition for applications requiring good strength properties up to 250 °C. The alloys are widely used for motorsport and aerospace gearbox casings, Elektron ZRE1 is used in aero engine components where improved creep resistance is required [90]. In the aeroengine industry, magnesium alloys are being used successfully in both civil and military aircraft [91]. Civil applications include intermediate casings for the engines and gearboxes, also in military aircraft, including the F16, Tornado and Eurofighter Typhoon, capitalise on the lightweight characteristics of magnesium alloys for transmission casings [63]. Physical properties of ZRE1 are specific gravity 1.80, coefficient of thermal expansion 26.8 x 10^{-6} K^{-1}, thermal conductivity 100 Wm^{-1} K^{-1}, specific heat 1040 J Kg^{-1} K^{-1}, electrical resistivity 73 n Ω m, modulus of elasticity 44 GPa, poisson's ratio 0.33, melting range 545-640 °C, and brinell hardness 50-60. Corrosion resistance, ASTM B117 Salt spray test, corrosion rate 3.5 mg/cm²/day [1]. Typical mechanical properties, tensile properties, 0.2% proof stress 110 MPa, ultimate tensile strength 160 MPa, elongation 3%, compressive, 0.2% proof stress 85-120 MPa, strength 275-340 MPa, shear stress 138 MPa, impact value, unnotched 6.1 7.4 J, notched 0.7-2.0 J. At low temperature (-196 °C), ultimate tensile strength 154 MPa, elongation 0.5 %, impact value 0.5 J [49].

Rzychoń et al., [89] investigated influence of pouring temperature on the microstructure, fluidity and mechanical properties of ZRE1 magnesium alloy. Casting in sand moulds has been done at different melt temperature (730, 780, 830°C). They also used long-term annealing at temperatures of 150, 200°C and 400°C up to 3000 h in order to determining of microstructural stability of the alloy. By microstructure investigated they found that as-cast ZRE1 alloy consist of α-Mg matrix and second phase crystallize along the grain boundaries. SEM observations of analyzed alloy reveal that the grain boundary second-phase shows a kind of massive morphology with bright contrast. The results of microanalysis by EDS showed that second phase was composed of magnesium, zinc and rare earth elements. Fluidity test of ZRE1 magnesium alloy showed that filling length increases slowly when the
pouring temperature increases from 730 to 780°C, but increases rapidly when the pouring temperature increases from 780 to 830°C. Their results showed also a very low solubility of rare earth elements in solid solution. The pouring temperature influences on the grain size of ZRE1 alloy, where the grain size rises with the increase of the casting temperature due to lower cooling rate. The hardness and ultimate tensile strength decrease slightly with the increase of casting temperature. The alloy poured from 730°C showed the highest UTS and hardness, which can be ascribed to finest grain size.

The high temperature creep performance of two magnesium alloys (AE42 and EZ33 (ZRE1)) developed for elevated temperature applications investigated by Fletcher et al., [92]. They used the nano-indentation creep technique (on the microscale) and neutron diffraction (on the macroscale) to study compressive creep behavior of extruded rods at room temperature and at 150°C. They found that the ZRE1 (EZ33) contained intermetallics (globular Mg2Zn1RE) exclusively on the grain boundaries. Thus, the intermetallics in the EZ33 were significantly more effective in pinning the grains during high temperature deformation. They also found that the ZRE1 (EZ33) alloy was ~35% harder and had a 30-43% higher elastic modulus than the AE42 alloy. Residual creep-produced strain in the AE42 alloy was significantly greater than that of EZ33. ZRE1 alloy contained fine and irregular intermetallics exclusively on the grain boundaries, which significantly enhanced the creep resistance of the alloy.

Rzychoń et al., [91], analyzed quantitative and qualitative characteristic of microstructure of Mg-3Zn-3RE (ZRE1). Their results show that microstructure of the alloy contains α-Mg matrix and discontinuous network intermetallic compound at the grain boundaries. SEM observations of analyzed alloy reveal that the grain boundary second-phase shows a kind of massive morphology with bright contrast, and EDS results showed that second phase was composed of magnesium, zinc and cerium.

It has been reported that the thermal analysis results of ZRE1 magnesium alloy showed, in the temperature range from 570 °C to 616 °C, the secondary intermetallic phase undergoes melting and the (α) solid solution crystals begin to melt, and that the liquids temperature is 697 °C. In addition, the secondary phase of the as-cast ZRE1 magnesium alloy begins to crystallize at 572 °C, he also found that the solidus temperature (end of solidification) is 552 °C [93].
2.3.4 Effect of Rare Earth Elements on Mg-Zn alloys

Rare Earths are added to magnesium alloys to improve the strength and creep-resistance [94]. Two groups of RE elements which considered for Mg alloys are high solubility (yttrium (Y), Gadolinium (Gd), Dysprosium (Dy)) and lower solubility (Neodymium (Nd), Cerium (Ce), Lanthanum (La)) and developed the properties of Mg alloys [18, 95].

The strength of Mg-RE alloys are enhanced by the zirconium (Zr) addition to refine grain size and the strength is further increased, if zinc (Zn) is added as well [18]. Among the most widely commercial Mg-RE alloys are gaining huge industrial due to their good ductility and strength because of the great refinement in microstructure by Zr addition, the Mg–Zn–Zr alloy system is one of precipitation strengthening alloys which have high strength and good ductility [96]. The properties of Mg-Zn-Zr alloys can be improved by addition of RE which lead to forming of ternary eutectic compound (MgZnRE) in the alloy [96, 97]. It had reported that the Ce addition refined the microstructure and increase the hardness of Mg-Zn alloy because the stable intermetallic compound MgZnxCx [98]. Moreover, Addition of RE also reduces porosity in casting and weld cracking, because the RE reduce the freezing range of the alloys [99]. In addition, the hard phases formed by RE addition lead to increasing the mechanical properties of the alloy as well. In general, the strengthening of magnesium alloy by the addition of RE resulted from grain boundary strengthening obtained by precipitates and solid solution [100-103].

2.3.4.1 Effect of Yttrium

Yttrium (Y) has a relatively high solid solubility in magnesium (12.4 wt%), and enhances high temperature strength and creep performance when combined with other RE metals. Figure 2.3 shows phase diagram of Mg-Y [1, 6, 104].
Figure 2.3: Magnesium-Yttrium phase diagram [6]

Yttrium is an element with a high solid solubility in magnesium and has the potential for age hardening. Initially, work was carried out on Mg-Y-Zn-RE alloys [105]. The zinc was added to reduce the solubility of the expensive yttrium. The mechanical properties were not as good as the Mg-Y-Nd-Zr alloys [106]. These alloys have better high temperature strength than QE alloys and furthermore better corrosion properties. It is possible, in order to reduce the costs, to use an yttrium-containing mischmetal with 75% Y and heavy earths, e.g., gadolinium and erbium [107].

About 4 to 5 wt.% of Zr is added to magnesium to form commercial alloys such as WE54 and WE43, where it imparts good elevated-temperature properties up to about 250 °C. The alloys containing Y, WE54 and WE43, are capable of resisting creep at operating temperatures up to 300 °C and at the same time exhibiting good room temperature properties. This development, driven by the needs of jet aircraft engines, resulted in a continuous improvement in strength and particularly elevated temperature resistance, culminating in current alloys such as WE43 (Mg-4%Y-3%RE (Rare Earth)-0.5%Zr) which have high strength and long term temperature stability at temperatures as high as 250 °C [66, 108].
The additions of Ce and Y additions reduced the grain sizes of microstructure, and Mg–Zn–Ce, Mg2Zn6Y (I-phase) and Mg2Zn3Y2 (W-phase) phases were formed in Mg–Zn–Zr alloys. In addition, that yield strength and ultimate tensile strength increased by addition of Ce and Y [109].

Qi et al., [110], reported that by adjusting the Zn to Y mass ratio they obtained various phases compositions, including Mg-Zn3, W-phase (Mg3Y2Zn3), I-phase (Mg3YZn6), and X-phase (Mg12YZn). The authors also reported that microstructures of the alloys are indicative of structural refinement in the base alloy after Y addition, and proffered that Y element has effect on grain refinement. They also found that Y addition lead to develop the strength of Mg–6Zn–1Mn alloy.

Xu et al., [111], reported that the tensile strength of Mg–5.5Zn–0.8Zr alloy had improved with 1.08 wt.% Y. Moreover, the grain sizes of the Mg–Zn–Y–Zr cast alloys significantly decreased with increased value of Y.

It has been reported that the addition of REs is the most promising method to increase ductility and improve the deformability of magnesium alloys. Furthermore, it was concluded that the addition of Y can promote the c+a slip of dislocations, which is activated and significantly contributes to the plastic deformation, leading to improve strength and ductility [42].

There are three kinds of ternary equilibrium phases in Mg–Zn–Y alloys in the Mg-rich region, which are X-phase (Mg12YZn), W-phase (Mg3Y2Zn3, cubic structure) and I-phase (Mg3YZn6) [111]. The formation of the secondary phases in Mg-Zn-Y-Zr alloys firmly depended on the mole ratio of Y to Zn. I-phase and X-phase are closely bonded with Mg matrix and can effectively retard the basal slip, and then strengthen the alloy greatly. W-phase is easily cracked during the tensile process, which degrades the mechanical properties [41].

2.3.4.2 Effect of Prasendium

Prasendium (Pr) is an RE metal used as an alloying agent with Mg to create high-strength metals used in aircraft engines. The Mg–Pr phase diagram (Fig.2.4) shows there is 1.7 mass % (wt%) solubility at the eutectic temperature 575 °C [112].
RE metals are added to Mg alloys either as mischmetal or as didymium. Mischmetal is a natural mixture of the rare earths containing about 50 wt% cerium, with the remainder being principally comprised of lanthanum and neodymium. Didymium is a natural mixture of approximately 85% neodymium and 15% praseodymium [10, 11]. Additions of the rare earths increase the strength of magnesium alloys at elevated temperatures. The reason of using mischmetal instead of pure elements is the similar behavior of RE elements while it is very economical to use mischmetals instead of pure rare earths. Recently developed alloys have contained separate rare earths. Individual rare earth metals have differing effects on the response of magnesium alloys to heat treatment with the mechanical properties generally increasing in the order of lanthanum, mischmetal, cerium and didymium [15].

Cui et al. [113] studied effect of Pr additions on Microstructure and mechanical properties of die-cast AZ91D magnesium alloy, by added 0.4, 0.8 and 1.2 wt% of Pr separately into the base alloy, were prepared by high-pressure die-casting technique. They investigated the effects of Pr on the microstructures of die-cast Mg-9Al based alloy by XRD and SEM. They found that the mass fraction of Pr at around 0.8% is considered to be suitable to obtain the optimal mechanical properties.
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