Solidification Behaviour and Microstructure Development of Mg-Al-RE (Ce and La) Alloys

A thesis submitted in fulfilment of the requirements for the degree of

Doctor of Philosophy

Charlotte Chiaw Wuen Wong

B.Eng(ChemEng)(Hons), Monash University

School of Engineering
College of Science, Engineering and Health
RMIT University

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This thesis is dedicated to all colleagues, friends, family and strangers who believed in me before anyone knew what they were believing in.

“Working hard is important but there is something that matters even more; believing in yourself.”

Harry Potter
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

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Abstract

The high specific strength of magnesium alloys makes them attractive for use in transport applications where potential weight savings can be significant. However, the most common magnesium alloys such as AZ91 (Mg-9Al-1Zn) and AM60 (Mg-6Al-0.3Mn) tend to suffer from poor creep resistance, limiting their use in high-temperature environments. The elevated temperature applications, such as powertrain components, offer significant potential for vehicle weight reductions. This limitation has stimulated the development of a number of high creep resistance magnesium alloys for powertrain components. Moreover, rare earth (RE) alloying additions in magnesium-aluminium based alloys are widely accepted to improve the creep resistance. The development of magnesium casting alloys depends significantly on the ability to control the as-cast microstructure. Microstructure in hyper-eutectic Mg-Al-RE (RE = Ce and La) alloys are analogous to those in A390 alloys used for pistons and cylinder liners. Both of these alloy systems form a large amount of hard secondary phase particles and fine eutectic similar to the composite structure. These attribute to improved properties of the alloys.

Previous studies have been performed to understand the effect of REs on the microstructure of Mg-Al-RE (AE) alloys, but different phases were reported. In addition, there is limited information about the effect of individual RE elements on AE alloys, especially on the hyper-eutectic region of these alloy systems. The lack of a comprehensive understanding of the microstructure evolution in AE alloys hinders the accuracy of thermodynamic predictions and hence limit the knowledge in magnesium alloy design and optimisation. Herein, the work described in this thesis aims to gain an improved understanding of the microstructural development of AE alloys.

The first objective in this research is to understand better the solidification sequence and thermodynamic predictions of the investigated alloys, which would be advantageous for the research and development of improved magnesium alloys. The second objective is to investigate the impacts of the individual RE (lanthanum and cerium) elements on the solidification path and microstructural development of AE alloys. Finally, the third objective of this thesis is to investigate the effects of cooling rates on the solidification behaviour and microstructure development of AE alloys. This includes the study of processing-microstructure relationships for the investigated alloys.

The investigations in this research study were carried out on a series of Mg-4Al-xCe and Mg-4Al-xLa alloys with “x” being the Ce and La concentration range from 4 wt.% to 13 wt.%. All
alloys were gravity cast into a wedge shape mould comprising two sections: permanent mould and sand mould. The use of a wedge mould with the combination of permanent and sand moulds allows a wide range of cooling rates to be explored within a single casting. The solidification behaviour and microstructure formation of these alloys were studied experimentally using both ex-situ and in-situ techniques. The as-cast microstructures of these alloys were studied by X-ray powder diffraction, scanning and transmission electron microscopy. The microstructure evolution was investigated and observed under a real-time solidification condition using in-situ synchrotron radiography. The effect of the cooling parameters on the microstructure and solidification behaviour was studied through computer-aided cooling curve analysis. The experimental results were compared with thermodynamic predictions calculated using the CALPHAD method.

There has been relatively little research done on the thermodynamic properties and phase equilibria of the Mg-Al-RE systems compared to other systems. In this study, thermodynamic calculations were utilised to understand the solidification sequence of the intermetallic phases through comparison with experimental data, which includes a real-time in-situ observation of solidification using the synchrotron radiation. It was determined that the thermodynamic predictions were contradictory to the experimental data. The discrepancy observed in this comparison, especially in the liquid-solid and solid-solid phase transformations, suggests that the Mg-Al-Ce and Mg-Al-La systems should be remodelled to improve the accuracy of the thermodynamic database.

The effects of alloying compositions on the solidification and microstructure development are also discussed in this thesis. The resultant microstructures from the as-cast alloys were characterised. The low RE content alloys, such as ALa44 and ACe44, exhibited a primary α-Mg phase surrounded by an interdendritic region of Mg and intermetallic(s). On the other hand, the high RE content alloys, such as ALa413 and ACE413, exhibited a primary intermetallic phase before the α-Mg grains developed. The morphology of the eutectic was also very distinct between the investigated alloys. During phase characterisation, there were distinct unknown peaks observed in the XRD measurements indicating a new type of intermetallic phase. After a detailed investigation, a new phase, (Al,Mg)_3La, was identified, which was found to be the dominant phase in the ALa44 alloys. The morphology and crystallographic information of this new (Al,Mg)_3La phase is also described in this thesis.
Another goal of this research is to study the relationships between the processing condition (i.e. cooling rate) and the resultant microstructure of the as-cast AE alloys. The effects of different cooling rates on the microstructures were analysed. Microstructural features, such as grain size and secondary dendrite arm spacing (SDAS) of the α-Mg phase, were measured and their influence on hardness has also been investigated. It was observed that the microstructural features contribute significantly to the hardness of the alloys. A generalised relationship between freezing time and SDAS using the commonly used empirical equation has been developed. In addition, microstructure-property relationships between yield stress and microstructure features (grain size and SDAS) for these alloys were discussed and established based on the Hall-Petch equation. This linear relationship with SDAS is observed to be similar to that obtained for average grain size, in which smaller SDAS and grain size leads to higher yield stress and hardness. Using these relationships developed in this study, it is possible to predict the hardness and microstructure features at a given cooling rate for the investigated alloys.

The consolidation of these objectives and the results of this research study can improve the knowledge base of AE alloys, especially from the perspective of solidification behaviour and microstructure development. The results should prove useful for alloy design and development that are targeted for specific applications, as well as for alloy optimisation to improve cast magnesium alloys.

*Keywords*: casting, as-cast magnesium alloys, microstructure, solidification process, cooling rate, Mg-Al-La system, Mg-Al-Ce system, thermodynamic prediction.
Publications and Achievements

Publications


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Chapter 1

Introduction
1 Introduction

1.1 Research significance and thesis motivation

Sustainable energy supply and climate change are two of the main challenges facing society today. The transport sector is responsible for approximately 19% of the total emissions contribution in Australia [1]. This makes the transportation industry a major source of environmental pollution, particularly carbon dioxide emissions produced by the consumption of fossil fuels by vehicles.

In recent years, there has been an increasingly higher demand for the automotive industry to improve vehicle efficiency using lightweight materials. According to the Australian Government Climate Change Authority (CCA) [2] and The Centre for International Economics (The CIE) [3], one of the least costly approaches to reducing emissions in Australia is to improve vehicle efficiency. This includes vehicle weight minimisation, as weight is strongly correlated with fuel consumption (Figure 1.1) as well as greenhouse gas (GHG) emissions. Currently, the ADR 79/04 is the minimum standard for new light vehicles in Australia [4]. This standard is based on the Euro 5 standards. The CCA also proposes that light vehicle emission standards will be introduced with effect from the year 2018 [2]. This has received considerable attention from many industries, particularly the automotive sector. Additionally, monetary penalties are placed on vehicle carbon dioxide emissions in some regions, such as the European Union (EU). These regulations are known as Euro 5/6, which set stricter emission limits on atmospheric pollutants for a new vehicle sold in the market [5]. Euro 7 emission standards will be implemented in 2020 with a further reduced CO₂ emission target [6]. In order to comply with the Euro emission standards, technology and manufacturing optimisations are essential.
The relationship between fuel consumption and vehicle mass shows that reducing vehicle mass can reduce the fuel consumption of the vehicles [7, 8]. The potential use of magnesium in applications such as powertrain and chassis component could be of great benefit in achieving high fuel efficiency.

As weight reduction is becoming increasingly more important in the automotive and transport sectors, magnesium is viewed as a favoured structural material due to its low-density and overall cost analysis [9]. According to Friedrich and Schumann [10], there is an estimated 5.5% reduction in fuel consumption for every 10% of weight reduction, including weight around the engine and gearbox. There are also other reports showing that for every 100 kg of vehicle weight reduction, fuel consumption can be reduced by 0.3-0.4 L per 100 km of travel [11-13]. Furthermore, fuel efficiency is emphasised in the light vehicle emissions standard in an Australia research report [2]. Figure 1.2 shows the current promising fuel efficiency improvement technologies and their potential emission reductions as a percentage [2]. Lightweight materials used for vehicle weight minimisation are currently a major area of interest within the field of automotive engineering. This approach could ultimately achieve emission reductions without compromising vehicle functionality [14].
Reducing vehicle weight by 10% can decrease the CO₂ emission by 6.5%.

In this research, magnesium alloys are studied as a potential material for vehicle weight minimisation. Compared with other structural materials, magnesium is approximately 35% less dense than aluminium, and at least four times lighter than steel (Table 1.1) [8, 15]. For this reason, magnesium alloys, as the lowest density structural metals [8], have become widely used for automotive applications in recent decades [16, 17].
Table 1.1 Physical and chemical properties of magnesium and other comparison materials [8, 18-22].

<table>
<thead>
<tr>
<th>Property</th>
<th>Unit</th>
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<th>Aluminium</th>
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<th>Titanium</th>
<th>Beryllium</th>
<th>Copper</th>
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<td></td>
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</tr>
<tr>
<td>a</td>
<td>nm</td>
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<td>0.4041</td>
<td>0.2866</td>
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</tr>
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<td>13</td>
<td>26</td>
<td>22</td>
<td>4</td>
<td>29</td>
</tr>
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<td>27.87</td>
<td>4.51</td>
<td>1.85</td>
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<td>Relative density at 20 °C</td>
<td>g/cm³</td>
<td>1.74</td>
<td>2.70</td>
<td>7.87</td>
<td>4.51</td>
<td>1.85</td>
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<td>295</td>
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<tr>
<td>Specific modulus</td>
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<td></td>
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<tr>
<td>Tensile strength</td>
<td>MPa</td>
<td>240 (for AZ91D)</td>
<td>320 (for A380)</td>
<td>350</td>
<td>900</td>
<td>565</td>
<td>210</td>
</tr>
<tr>
<td>Melting point</td>
<td>°C</td>
<td>650</td>
<td>660</td>
<td>1535</td>
<td>1678</td>
<td>1289</td>
<td>1083</td>
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<tr>
<td>Boiling point</td>
<td>°C</td>
<td>1090</td>
<td>2520</td>
<td>2862</td>
<td>3289</td>
<td>2472</td>
<td>2563</td>
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<tr>
<td>Thermal conductivity (at 20-100 °C)</td>
<td>W·m⁻¹·K⁻¹</td>
<td>156</td>
<td>238</td>
<td>78</td>
<td>26</td>
<td>194</td>
<td>397</td>
</tr>
<tr>
<td>Coefficient of thermal expansion at 0-100 °C</td>
<td>10⁻⁸ K⁻¹</td>
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<td>23.5</td>
<td>12.1</td>
<td>8.9</td>
<td>12.0</td>
<td>17.0</td>
</tr>
<tr>
<td>Mean specific heat 0-100 °C</td>
<td>J kg⁻¹K⁻¹</td>
<td>1038</td>
<td>917</td>
<td>456</td>
<td>528</td>
<td>2052</td>
<td>386</td>
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<tr>
<td>Electrical resistivity at 20 °C</td>
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<td>10.10</td>
<td>54.00</td>
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</tr>
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</table>

1.1.1 Magnesium alloy designation

Magnesium alloys are designated according to the American Society for Testing and Materials (ASTM) [23-25] nomenclature. This coding system contains three parts, consisting of a letter-number-letter approach, and the designations are based on the chemical compositions of the alloys [25]. The first part of the system involves alphabetic letters indicating the two principal alloying elements. The second part represents the weight percentage of the two alloying elements as numbers. These numbers are rounded off to the nearest integer. In the third and last part of this alphanumerical ASTM method, an alphabetical letter indicates the generation of the magnesium alloy [23-25]. For instance, AE47X indicates the system is a magnesium alloy with aluminium and rare earth (RE) elements of 4 wt.% and 7 wt.%, respectively, and the “X” in the third part of the system indicates that the alloy status is currently experimental.

In addition to the designation system for magnesium alloys, the ASTM has also developed a system to identify various tempers of an alloy [23, 24]. This coding method also consists of alphabetical and numerical letters. The temper designation is located at the back, following the magnesium alloy designation with a hyphen to identify its temper status. For example, AZ91C-
where “F” indicates die-cast, which means this alloy is in the as-cast condition [23, 24]. Table 1.2 lists the abbreviations for the most commonly used alloying elements.

Table 1.2 ASTM abbreviations for alloying elements in magnesium alloys [23, 25].

<table>
<thead>
<tr>
<th>Code</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Aluminium</td>
</tr>
<tr>
<td>B</td>
<td>Bismuth</td>
</tr>
<tr>
<td>C</td>
<td>Copper</td>
</tr>
<tr>
<td>D</td>
<td>Cadmium</td>
</tr>
<tr>
<td>E</td>
<td>Rare Earth</td>
</tr>
<tr>
<td>F</td>
<td>Iron</td>
</tr>
<tr>
<td>G</td>
<td>Magnesium</td>
</tr>
<tr>
<td>H</td>
<td>Thorium</td>
</tr>
<tr>
<td>J</td>
<td>Strontium</td>
</tr>
<tr>
<td>K</td>
<td>Zirconium</td>
</tr>
<tr>
<td>L</td>
<td>Lithium</td>
</tr>
<tr>
<td>M</td>
<td>Manganese</td>
</tr>
<tr>
<td>N</td>
<td>Nickel</td>
</tr>
<tr>
<td>P</td>
<td>Lead</td>
</tr>
<tr>
<td>Q</td>
<td>Silver</td>
</tr>
<tr>
<td>R</td>
<td>Chromium</td>
</tr>
<tr>
<td>S</td>
<td>Silicon</td>
</tr>
<tr>
<td>T</td>
<td>Tin</td>
</tr>
<tr>
<td>V</td>
<td>Gadolinium</td>
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<td>W</td>
<td>Yttrium</td>
</tr>
<tr>
<td>Z</td>
<td>Zinc</td>
</tr>
</tbody>
</table>

In this research study, individual rare earth alloying, in particular lanthanum and cerium, will be designated as “Ce” and “La” using the ASTM nomenclature format. For example, a Mg-4Al-4Ce alloy is designated as ACe44, and a Mg-4Al-4La alloy is designated as ALa44.

1.1.2 The motivation for magnesium alloy applications

1.1.2.1 Magnesium alloy applications

In the past, magnesium has been used mainly as an alloying addition, especially in aluminium alloys [9]. Between 1998 and 2013 (Figure 1.3), there has been a trend in the growth of
magnesium alloy die-castings for automotive applications. This has accounted for approximately 35% of total magnesium usage, which is similar to the amount used in aluminium alloying for 2013 [9, 26]. Magnesium die-casting is largely used in the automotive sector and is widely used by European car manufacturers [9]. Nevertheless, steel and aluminium are currently the dominant alloys for automotive applications due to some limitations and challenges with magnesium alloys. Despite the greater density of steel and aluminium compared to magnesium alloys, they possess higher strength, corrosion resistance and creep strength, which makes them the preferred materials for many automotive applications. In order to develop an ideal lightweight material such as a magnesium alloy with high strength and good mechanical properties, further research is needed. Because casting, in particular high pressure die-casting (HPDC) and gravity casting, is the dominant fabrication method for magnesium alloy production [7, 15], it is particularly important to gain an in-depth understanding of the solidification behaviour and microstructure development, which contribute to the mechanical properties of cast magnesium alloys.

![Figure 1.3 Magnesium uses in 1998 and 2013 [9, 26].](image)
Commercial vehicles consist of four modules: the drive train, interior, body and chassis. Generally, automotive die-castings are categorised into powertrain, bracketry, and structural applications [9]. Figure 1.4 shows examples of each of the three main types of applications. Magnesium-based alloys are used for automotive applications in some of these modules to replace steel and aluminium parts [27]. These replacement parts include steering wheels, steering column components, instrument panels, seat frames, gear boxes, air intake systems, gearbox housings, tank covers, among others [28].

![Image of automotive components]

In present automotive applications, there are four common commercial systems of die-cast magnesium alloys: Mg-Al-Zn-Mn (AZ series), Mg-Al-Mn (AM series), Mg-Al-Si (AS series), and Mg-Al-RE (AE series) [29]. Die-cast Mg-Al-Zn-Mn and Mg-Al-Mn alloys, such as AZ91D and AM60B, are the most commonly used magnesium alloys for room temperature structural automotive applications [9]. These applications often require alloys with high strength and ductility; ductility is especially important for structural applications because the ability to absorb energy during a crash is critical [9]. In contrast, powertrain components often
encounter elevated temperatures, hence creep resistant alloys are necessary for these applications [9].

Despite the popularity of the AZ and AM alloys that have been used in industry, there is an apparent disadvantage to using these alloys in powertrain parts that operate at elevated temperatures above 130 °C [16, 29]. Due to this limitation, die-cast Mg-Al-Si (AS series) alloys were invented for use at temperatures above 150 °C where creep resistance is necessary. AS41A, which can operate at temperatures up to approximately 150 °C, was successfully used in crankcases of air-cooled automotive engines, fan housings by Volkswagen as well as clutch pistons by General Motors [29]. Despite the high melting temperature of the Mg₂Si precipitates in AS alloys that exhibit improved creep resistance, the alloy is difficult to die-cast [30]. Using the effects of rare earth additions in magnesium-aluminium based alloys, which were first discovered in the 1930s [31], die-cast AE41 and AE42 were found to have good creep resistance and better castability compared to AS alloys [29, 31]. The creep resistance of AE alloys is further improved, especially when the aluminium content is low in the alloy [29, 31]. Other alloys developed specifically for elevated temperature applications also include AJ62, MRI-153 (Mg-Al-Ca-Sr based alloy), AS31, and AE44 [9].

1.1.2.2 Market trend of magnesium alloys

Historically, German-based car manufacturers have been the leaders in adopting magnesium die-cast components. The experience of these manufacturers has proven the weight saving and performance benefits of using magnesium alloys in automotive applications [9]. There was an upward trend showing magnesium usage grew throughout the 1930s and continued to grow exponentially during World War II, but it reduced dramatically again after the War to 10,000 t per annum [28]. However, with the introduction of the Volkswagen Beetle, magnesium consumption in the automotive industry increased to a peak in 1971 with an annual production volume of 42,000 t [10, 15]. In those eras, AS41 and AZ81 alloys were widely used in air-cooled engines and gearboxes; the vehicle parts with magnesium alloys made up approximately 20 kg of the vehicle weight [10].

As technology advanced, magnesium alloys could not keep up with the greater power requirements for engines with higher operating temperatures and loads. The consumption of magnesium for structural applications declined dramatically after the 1970s. In the mid-1970s, the United States made a major effort to reduce their dependency on imported oil due to the fuel crisis, during which the import of fuel reduced to 35 % in 1973 [32]. Following on,
Corporate Average Fuel Economy (CAFE) legislation was introduced in 1978, and the regulations enforced vehicle makers to produce vehicles with better fuel efficiency, and hence the greater use of lightweight materials was seen as a result of the regulation enforcement [32]. In 1993, Ford, Chrysler and General Motors consumed a total of 14,282 t of magnesium, which represented approximately 70% of the annual magnesium casting in North America [29, 33]. In 1994, the consumption of magnesium had reached 228,000 t globally [28]. From 1998, the interests in magnesium applications were renewed again due to environmental regulations as well as high oil prices. This renewed interest led to an increase in magnesium applications to 360,000 t per annum [28].

It has been shown that magnesium castings are increasingly being used in industry by the major automotive companies, including GM, Ford, Volkswagen, Audi and Toyota [15, 34-39]. The major user of magnesium die-cast components is the European automotive industry; where approximately 50,000 t of magnesium die-cast components are produced each year [9, 40]. Currently, the AZ and AM series alloys are the most commonly used magnesium alloys in the commercial automotive applications, due to their high strength, elongation and good manufacturability, e.g. castability and machinability [28, 41]. Apart from the applications in the automotive industry, magnesium alloys have attractive properties, which make them suitable for use in sports equipment, industrial tools and electronic equipment such as mobile phone housings and bicycle frames [28, 42].

1.2 Magnesium alloy processing and manufacturing

1.2.1 Elemental magnesium

Magnesium is the seventh most abundant metal element on earth [43] and the third most abundant structural metal after aluminium and iron [44]. It is an alkaline earth element located in Group II of the periodic table. Magnesium has a hexagonal close-packed (HCP) crystal structure, and it is relatively soft and has a low elastic modulus [7, 28, 45]. It is the lightest structural metal with a density of 1.738 g/cm³, which makes it attractive for automotive applications. Apart from its low density, it has good strength to weight ratio as well as good castability [46]. The physical properties of pure magnesium are shown in Table 1.3. The cost is relatively low due to the abundance of the element and the extraction process for magnesium is less costly compared to other elements, such as titanium. Hence, magnesium alloys have become one of the most promising lightweight materials for automotive applications [47].
Table 1.3 Physical properties of magnesium [48].

<table>
<thead>
<tr>
<th>Physical properties of magnesium</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting point</td>
<td>650 °C±2</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>0.37 Mj/kg</td>
</tr>
<tr>
<td>Latent heat of fusion</td>
<td>5.25 Mj/kg</td>
</tr>
<tr>
<td>Heat of combustion</td>
<td>25.1 Mj/kg</td>
</tr>
<tr>
<td>Specific heat</td>
<td></td>
</tr>
<tr>
<td>at 20 °C</td>
<td>1030 j kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>at 600 °C</td>
<td>1178 j kg⁻¹ K⁻¹</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td></td>
</tr>
<tr>
<td>at 20 °C</td>
<td>4.45 mΩ/cm</td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td></td>
</tr>
<tr>
<td>at 25 °C</td>
<td>155 W m⁻¹ K⁻¹</td>
</tr>
<tr>
<td>The linear coefficient of thermal expansion</td>
<td></td>
</tr>
<tr>
<td>at 20 °C</td>
<td>25.2x10⁶ K⁻¹</td>
</tr>
<tr>
<td>at 20-300 °C</td>
<td>27-28x10⁶ K⁻¹</td>
</tr>
<tr>
<td>Density (solid)</td>
<td></td>
</tr>
<tr>
<td>at 20 °C</td>
<td>1738 g/cm³</td>
</tr>
<tr>
<td>at 600 °C</td>
<td>1622 g/cm³</td>
</tr>
<tr>
<td>Density above 650 °C</td>
<td></td>
</tr>
<tr>
<td>(liquid), g/cm³</td>
<td>1.834 - 2.647x10⁻⁴ T</td>
</tr>
<tr>
<td>Standard redox potential</td>
<td>-2.372 V</td>
</tr>
</tbody>
</table>

1.2.2 Magnesium alloying process

Although magnesium is readily available commercially with a purity exceeding 99.8%, it is rarely suitable to be used for engineering applications in its unalloyed form [8, 23]. This is because pure magnesium is an overly soft material [48]. Therefore, magnesium is alloyed with other elements in commercial applications.

Alloying elements are included to improve the properties, in particular by grain refinement, dispersion strengthening, solid solution hardening and precipitation hardening [49]. A wide variety of properties are affected and often improved by alloying additions. This is usually an effective way of increasing both the manufacturability and product properties, but can reduce some properties such as ductility of the alloys [24, 50-52]. It is also known that castability is significantly affected by the alloy composition [13, 53, 54]. The selection criteria for alloying
elements involve various considerations, such as atomic size, development of intermetallic phases, and precipitation sequence.

In solid solution strengthening, the alloying elements (solute) completely dissolve in the base metal (solvent). The solute atoms provide strengthening effects by (i) the misfit of atoms relative to the packing of the matrix atoms, and (ii) the variance in elastic moduli between the solute and solvent atoms [49]. In addition, it is also known that solid solution elements can improve creep resistance under the condition that the solute is able to: (i) increase the homologous temperature, (ii) enhance elastic modulus, or (iii) reduce diffusivity as described in the following equation [49],

\[ \dot{\varepsilon} = S(\sigma/E)^\eta D \]

where \( \dot{\varepsilon} \) is steady-state creep rate, \( S \) is a structured term such as grain morphology, dislocation density, distribution and others, \( \sigma \) is stress, \( E \) is elastic modulus, \( D \) is self-diffusivity, and \( \eta \) is a stress component.

Precipitation or age hardening is another strengthening process in alloys. This type of mechanism occurs when the solid solubility reduces with decreasing temperature. The interaction of glide dislocations with the precipitates can increase the yield stress, as per the following equation [49, 55],

\[ \tau_{\text{yield}} = \frac{(2aGb)}{1} + \tau_a \]

where \( \tau_{\text{yield}} \) is the yield strength of the precipitation hardened alloy, \( \tau_a \) is the yield strength of the matrix without precipitates, \( (2aGb/1) \) is the stress required for the dislocations to bypass the precipitates. Generally, precipitates alone are not adequate for alloy strengthening, unless the precipitates are fully coherent, are finely dispersed and are able to resist coarsening [49].

Currently, there are approximately 25 metals identified to be suitable as alloying elements for magnesium alloys based on their atomic size [41]. However, there are only approximately ten elements considered to be favourable alloying elements for magnesium alloys [24]. The major alloying elements and their effects in magnesium alloys have been analysed as shown in Table
1.4. On the other hand, copper, nickel and iron are classified as harmful contaminants for magnesium alloys which need to be removed to retain good corrosion resistance [24].

Table 1.4 The major alloying elements and their effects in magnesium alloys [24, 50-52].

<table>
<thead>
<tr>
<th>The major alloying elements and their effects in magnesium alloys</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
</tr>
<tr>
<td>Zinc</td>
</tr>
<tr>
<td>Manganese</td>
</tr>
<tr>
<td>Yttrium</td>
</tr>
<tr>
<td>Silver</td>
</tr>
<tr>
<td>Cerium</td>
</tr>
<tr>
<td>Neodymium</td>
</tr>
<tr>
<td>Heavy Rare Earth (e.g. Scandium)</td>
</tr>
<tr>
<td>Zirconium</td>
</tr>
</tbody>
</table>

1.2.3 Die-casting process

In material fabrication, there are several material selection criteria required to be taken into account in order to be deemed as a commercially viable material. These criteria include the in-service conditions, deterioration of material properties, ease of processing, performance and cost of fabrication [45]. Fabrication processes significantly alter alloy properties and further alterations may also be induced by heat treatment.

The production of magnesium alloys is generally dominated by casting [56] and wrought processes [57]. Alloys produced using wrought methods are generally stronger and have higher ductility compared with cast alloys. However, because high forming temperatures are required in order to activate the slip systems within the HCP structure of magnesium, higher energy consumption is needed during wrought processing, increasing production costs and resulting in poor control of surface appearance [8]. In contrast, casting is a relatively simple process. It has been shown that the manufacture of magnesium components is dominated by casting, with approximately 98 % of structural parts being castings [20]. Although the current dominant
production route for magnesium parts is HPDC, gravity sand-casting and permanent-mould casting are also widely used in the production of a variety of structural components [15].

HPDC technology includes cold chamber and hot chamber machines. The cold chamber machines are more beneficial for large castings, whereas the hot chamber machines are used for smaller castings and involve shorter cycle times [7]. The mechanisms of the hot and cold chamber processes are explained elsewhere [15]. Magnesium alloys are particularly suitable for HPDC because of their high fluidity, which makes them suitable for complex mould shapes and thin walled castings. Magnesium alloys containing rare earth elements possess even greater fluidity [58], as shown in Figure 1.5. Because magnesium contains low specific heat per unit volume, the cycle time of casting is shorter. It is also reported that some magnesium parts can be die-cast up to 50 % faster compared to the same parts cast in aluminium [29]. Due to the low density of magnesium alloys, moderate gate pressure is used to achieve the same effect as high gate pressure for other alloys during HPDC. The low solubility of iron in magnesium alloys also helps to minimise the tendency of sticking with steel tooling [7, 15].

![Figure 1.5 Fluidity of Mg-Al-xRE alloys [58].](image)

During HPDC, the molten liquid metal is poured into a mould with high pressure and high velocity [59] through a narrow flow gate. This allows the molten liquid metal to cool and solidify under pressure and at high cooling rates (100 to 1000 °C/s), which results in a fine grained microstructure [41]. Pure magnesium melts at 650 °C [28] and the melting temperature of a magnesium alloy varies in accordance with the alloying elements added. This method is suitable for low melting temperature metal alloys, such as magnesium alloys. It is well known that HPDC is a preferred method for magnesium alloy production at commercially viable scales. Table 1.5 lists the benefits and limitations of magnesium alloys produced by high
pressure die-casting. Thin-walled high pressure die-casting is well established and used to produce magnesium alloys in applications where high strength is not critical.

Alternatively, magnesium alloys can be cast with thicker walls where higher strengths are required [15]. Interestingly, a previous study shows the strength at elevated temperatures, ductility and creep resistance of the alloy can also improve using thin-walled high-pressure die-castings [60]. Table 1.6 compares the common design parameters for magnesium and aluminium die-castings in the automotive industry.

Table 1.5 The advantages and disadvantages of high pressure die-cast for Mg alloys [28].

<table>
<thead>
<tr>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>High productivity</td>
<td>Gas pores entrapment</td>
</tr>
<tr>
<td>High precision</td>
<td>Limited mechanical properties</td>
</tr>
<tr>
<td>High-quality surface</td>
<td>Limited range of alloys</td>
</tr>
<tr>
<td>Fine cast structure</td>
<td>Poor creep resistance</td>
</tr>
<tr>
<td>Higher casting rate</td>
<td>High cost for creep resistance alloys</td>
</tr>
<tr>
<td>Longer life with steel ingots</td>
<td>Limited castability for creep resistance alloys</td>
</tr>
<tr>
<td>Energy saving due to lower heat content</td>
<td>Heat treatment not applicable</td>
</tr>
<tr>
<td>Good machinability</td>
<td>Unsuitable for welding</td>
</tr>
<tr>
<td>High fluidity of melt</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.6 Design parameters for magnesium and aluminium die-casting [15].

<table>
<thead>
<tr>
<th>Material</th>
<th>Magnesium die-casting</th>
<th>Aluminium die-casting</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimensional tolerance (mm/mm)</td>
<td>±0.001</td>
<td>±0.002</td>
</tr>
<tr>
<td>Draft angle (°)</td>
<td>0-1.5</td>
<td>2-3</td>
</tr>
<tr>
<td>Minimum wall thickness (mm)</td>
<td>1-1.5</td>
<td>2-2.5</td>
</tr>
<tr>
<td>Casting/moulding cycle time (unit)</td>
<td>1.0-1.4</td>
<td>1.4-1.6</td>
</tr>
<tr>
<td>Typical die life (×1000 shots)</td>
<td>250-300</td>
<td>100-150</td>
</tr>
<tr>
<td>Trimming cycle time (unit)</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Machinability</td>
<td>Excellent</td>
<td>Good</td>
</tr>
<tr>
<td>Welding/joining</td>
<td>Fair</td>
<td>Good</td>
</tr>
<tr>
<td>Surface finishing</td>
<td>Excellent</td>
<td>Excellent</td>
</tr>
<tr>
<td>Recyclability</td>
<td>Good</td>
<td>Good</td>
</tr>
</tbody>
</table>

Gravity casting, in particular sand-casting, is helpful when the casting geometry is large. Sand-casting of magnesium alloys is similar to other cast metals. However, a suitable inhibitor should
be used in the sand mould mixtures to prevent reactions between the molten alloy and sand mixtures [15]. On the other hand, permanent mould casting is very similar to sand-casting. The difference between these two processes is that permanent mould casting involves a metal mould instead of a sand mould. In addition, permanent mould casting generally produces a better surface finish and better mechanical properties due to faster solidification [15].

Additional treatments, known as thermal processing, may also be used to further alter the mechanical properties of the metal alloy by recrystallisation of microstructures. Processes such as annealing, heat treatment and precipitation hardening are part of thermal processing [45]. Research also shows that gravity casting and low pressure die-casting followed by heat treatment can improve the mechanical properties of the alloys. Although it is known that further creep improvement can be achieved by ageing the alloy in some cases [60], the study conducted by Regener et al. [61] reveals that the annealing process does not lead to significant effects on the microstructural stability and hence the creep performance of the as-cast AE42 alloy.

Despite the apparent benefits of die-cast magnesium alloys, steel and aluminium remain the dominant materials for the automotive industry. There are drawbacks to magnesium die-casting including defect formation, such as porosity and hot tearing issues, which require resolution to improve the performance and productivity of magnesium alloys.

A fundamental understanding of the solidification behaviour and consequent microstructure development in cast alloys is important to controlling the mechanical properties of the final product and minimising defect formation, as demonstrated in a previous study [62] of aluminium and magnesium castings. This is because there is a complex relationship between microstructure development and processing conditions (one can affect the other), particularly when the aim is to produce as-cast products such as HPDC components. Hence it is important to understand the influence of process parameters, such as cooling profile, on the solidification pathways and phase selection in different alloys so that properties such as creep resistance can be optimised. Currently, the effects of cooling rate on microstructure development in the AE series of alloys are not well understood, hence this is a focus of the research presented in this thesis.

1.2.4 Microstructure in cast alloys

There are three zones developed during solidification of cast alloys as shown in Figure 1.6: the chill zone, columnar zone, and equiaxed zone [63]. In casting, molten metal is poured into the mould and contact with the cold mould wall causes it to be rapidly chilled below the liquidus
temperature. This is known as the chill zone. Because of the rapid cooling near the cold mould wall, multiple solid nuclei form on the wall and begin to grow into the liquid. Following the chill zone, the temperature gradient decreases and the crystals developed from the chill zone continue to grow dendritically in specific crystallographic directions into the liquid, which is known as the columnar zone. Then, it continues to grow and form equiaxed grains that are randomly oriented at the core of the cast. The final stage is the equiaxed zone [64].

![Figure 1.6 A typical microstructure of a cast ingot [63].](image)

It is well established that the morphology of constituent phases can be governed by the casting processing parameters [65]. Generally, in die-casting, the grains formed and located near the “skin” region of the casting are smaller compared to the grains formed and located within the “core” region. This can be explained by the rapid solidification rate at the ”skin” region as a consequence of rapid heat extraction through the walls of the mould [13, 66]. In addition, larger grains, which can grow up to 100µm or more [13, 66], may form in the “core” region of the casting and are known as externally solidified grains (ESG) [13, 67]. Although it is known that the properties of die-cast alloys rely on the microstructure development, Gertsman et al. [65] emphasised that the fundamental factors of the microstructure formation and evolution during die-casting remain unclear, and further study is required to understand them fully.

### 1.3 The Mg-Al-RE systems

In recent years, the Mg-Al-RE (AE) alloys have become promising materials for creep resistant light-weight magnesium alloys. Previous studies have confirmed that the AE series of magnesium alloys possess high strength and creep resistance [68]. In addition, a previous study reported a decrease in creep resistance of AE42 above test temperatures of 175 °C [69]. However, the AE42 alloy tends to deteriorate rapidly at temperatures above 150 °C [70] along
with some issues with hot tearing [71]. Further improvement can be seen by increasing the concentration of rare earths, and hence AE44 was developed [72]. Figure 1.7 shows the creep behaviour of AZ91, AE44 and ACe44 alloys at 150 °C under a stress of 50 MPa and at 200 °C under a stress of 70 MPa. It is apparent that the AE44 and ACe44 alloys have much greater creep performance than the AZ91 alloy. In addition, Figure 1.8 shows the creep strain rate for AZ91, AS41, AE41 and AE42 at 150 °C under a tensile load of 50 MPa. It can be seen from these figures that the creep resistance of AE alloys outperforms the other alloy systems. In addition, it is proven that the rare earth elements contribute to increased hardness, as shown in Figure 1.9.

![Figure 1.7 Tensile creep curve for HPDC AZ91, AE44 and ACe44 [73].](image)
The microstructure and mechanical behaviour of alloys can be affected by the type of rare earth elements to a certain extent [58, 73, 75-80]. To date, previous studies have been conducted on cerium, lanthanum, praseodymium and neodymium [58, 73-83]. It is believed that different rare earth alloying elements can lead to different microstructure stability and mechanical properties. For example, further improved creep and tensile properties can be obtained by substituting the rare earth content of the alloy from cerium to lanthanum [84]. In addition, different rare earth elements with various concentrations have different effects on improving tensile yield strength of the alloys at different operating temperatures, as shown in Figure 1.10. This is because higher rare earth alloying concentrations lead to a greater volume of intermetallic phases, and hence better creep properties. For example, the AE44 alloy possesses
better creep resistance compared to the AE42 alloy [85]. Further confirmation of this explanation was performed using transmission electron microscopy (TEM), in which precipitates were identified within the \( \alpha \)-Mg grains of a permanent-mould cast Mg-1.3RE alloy after aging [86]. Additionally, X-ray powder diffraction (XRD) analysis was conducted to confirm the benefits of phase precipitations [87, 88]. Currently, the new AE series alloys with their high temperature creep resistant properties have been successfully used as cylinder head covers and in oil pans (Figure 1.11) [78, 89]. These enhanced alloys have been proven to have a working temperature of up to 150 \( ^\circ \)C [89], higher than the AZ and AM series alloys.

\[\text{Figure 1.10 Effect of rare earth contents on TYS of AE alloys [51].}\]

\[\text{Figure 1.11 High performance die-cast AE alloys are selected to produce (a) cylinder head cover of the high power diesel engine and (b) oil pan for cars [78, 89].}\]
Chapter 1 Introduction

It is well known that rare earths contribute positively as an addition for improving the casting and properties of Mg-Al based alloys [90, 91]. The evidence presented in this section suggests that Mg-Al-RE alloys have great potential to improve creep resistance as well as the strength and ductility of the alloy.

1.3.1 Thermodynamic database for Mg-Al-RE systems

Development of a reliable thermodynamic database, especially for multi-component alloy systems, requires a combination of experiments and computational thermochemistry [91-93]. A reliable thermodynamic database and phase diagram is important in all parts of material design and development because the phase diagram can predict the solidification behaviour of a specific alloy composition. In addition, the database contains critical information such as phase relationships and phase stability under given conditions.

To date, little effort has been made to construct reliable phase diagrams in Mg-Al-RE systems. Many experimental studies published on the phase equilibria of Mg-Al-RE systems are contradictory [94-97]. The calculated phase diagram is in substantial disagreement with the experimental results [98, 99]. The discrepancy among the published results and limited experimental data encourages a new experimental investigation for the verification and reassessment of the Mg-Al-RE systems.

1.4 Research aims and objectives

In order to continue increasing magnesium alloy applications, it is important to have alloys that possess good mechanical properties, such as strength and ductility, good creep resistance, adequate corrosion resistance, good castability and affordable cost. The thermal stability of the intermetallic phases and the fine eutectic structure in the AE alloys is an especially important contribution to the creep resistance. However, it has been a challenge to predict the microstructure development, especially when solidification takes place under rapid, non-equilibrium conditions, such as in high pressure die casting. In addition, microstructure in hyper-eutectic Mg-Al-Ce and Mg-Al-La alloys are analogous to that of the A390 Al-17wt.%Si based alloys, used for piston and cylinder liners. These alloys systems contain large amounts of hard second phase particles that can contribute to increased strength and wear resistance.

In the commonly used Mg-Al based alloys the large fraction of Mg$_{17}$Al$_{12}$ in the eutectic makes hyper-eutectic compositions extremely brittle and impractical. Mg-Al-Ce and Mg-Al-La based
alloys, however, have ductile eutectics with relatively small fractions of intermetallic phase. This opens the possibility for in-situ composites with Al-RE and Mg-RE phases playing an analogous role to Si, Mg$_2$Si and Al-$(\text{Cu, Ni})$ based intermetallic phases in A390 and similar Al based alloys.

Currently, the hyper-eutectic regions of Mg-Al-RE systems have been seldom investigated. This research aims to provide an important opportunity to advance the understanding of solidification behaviour and microstructure development of hypo- and hyper-eutectic Mg-Al-RE alloys. The findings in this study should make an important contribution to the field of magnesium alloys.

The objectives of this research are:

1. To characterise and compare the microstructure and intermetallic phase development in Mg-Al-Ce and Mg-Al-La alloys.
2. To determine the sequence of intermetallic phases, developed during solidification processes by combining both the experimental data and thermodynamic predictions, and to review the inconsistencies in the thermodynamic databases for Mg-Al-Ce and Mg-Al-La alloys.
3. To Investigate the effects of rare earth alloying elements and their concentrations on the microstructure development of Mg-Al based alloys.
4. To understand the solidification behaviour of Mg-Al-Ce and Mg-Al-La alloys at different cooling rates using thermal analysis technique.
5. To correlate the relationship between processing-microstructure-properties for Mg-Al-Ce and Mg-Al-La alloys.

1.5 Thesis outline

The work presented in this thesis includes six detailed studies of a range of Mg-Al-La and Mg-Al-Ce alloys. The microstructural evolution and solidification behaviour were investigated using both in-situ and ex-situ experimental approaches. The thermodynamic software package, Pandat® with the PanMagnesium 2018 [100] database, has also been used to investigate the solidification characteristics of magnesium alloys. Comparisons have been made between thermodynamic predictions and experimental results to better understand the solidification behaviour and microstructure development of Mg-Al-RE alloys.
This thesis is divided into ten chapters and work presented in individual chapters is explained as follows. Chapter 2 presents a review of the existing literature concerning the microstructural evolution and solidification behaviour of Mg-Al-RE alloys (where RE can be mischmetal, or individual cerium or lanthanum alloying additions) with a focus on the intermetallic phases, such as Al$_2$RE and Al$_{11}$RE$_3$ that are commonly reported in these alloys. The key feature of these phases is the effect on the creep performance of the alloys. Whilst the intermetallic phases have been characterised in these alloys, comparatively little information is available regarding the effect of individual rare earth alloying additions on the associated microstructure.

Chapter 3 describes the various materials and experimental methodologies used in this study. This includes the gravity wedge casting process, thermal analysis, and sample preparations for microscopy work as well as for X-ray powder diffraction and synchrotron radiography. The microstructure characterisation is also described in this chapter. The individual experimental techniques are also explained in detail in the following chapters, some of which are published in peer-reviewed journals (Chapters 4, 5 and 6).

The results of the individual research topics of this thesis are discussed in Chapter 4 to 9. An investigation of Mg-Al-Ce system is presented in Chapter 4. The microstructure in ACe310 and ACe412 alloys were characterised and compared with thermodynamic predictions.

During the investigation of Mg-Al-La system, a new intermetallic phase, (Al,Mg)$_3$La, has been identified, which is detailed in Chapter 5. The crystal structure has been resolved using high-resolution synchrotron X-ray powder diffraction.

In Chapter 6 the Mg-Al-La system is investigated using a combination of synchrotron radiography, thermal analysis and microstructural characterisation. The solidification of an ALa314 alloy was determined and compared with thermodynamic predictions.

The investigations into the Mg-Al-Ce and Mg-Al-La systems indicate that the intermetallic phases are not the same as commonly reported in the literature. In Chapter 7 and 8 comparative studies of alloys from these systems are therefore investigated. The role of individual rare earth elements on phase selection is also discussed in Chapter 8.

In Chapter 9 the results from previous chapters are rationalised, and quantification of key microstructural features of the Mg-Al-RE alloys are made to assist with the discussion of the influence of different rare earth elements and the effects of different cooling rates on the
properties of the investigated alloys. The processing – microstructure – property relationships are developed for the investigated alloys in this study.

Finally, Chapter 10 summarises the overall findings of this thesis and outlines several recommendations for future work.
1.6 References


27. N.D. Saddock, et al., *Solidification and microstructure of Mg-Al-(Ca, Sr, Ce, La) ternary alloys*. Essential Readings in Magnesium Technology, 2005: p. 199-204.


Chapter 1 Introduction


Chapter 1 Introduction


Chapter 1 Introduction


2 Chapter 2: Literature review

This chapter begins with an introduction to the phase diagrams of the binary Mg-Al, Mg-RE and Al-RE systems as well as the ternary Mg-Al-RE systems. Then, the solidification behaviour and microstructural features of magnesium alloys in these systems are discussed, including the current literature on intermetallic phase selection and solidification sequence during cooling in Mg-Al-RE alloys. Lastly, because the alloy properties are strongly influenced by the microstructure, which is controlled by the processing conditions, the effect of the cooling rate and the roles of rare earth (RE) alloying elements on the formation of different phases are outlined in detail, emphasising the importance in phase selection for Mg-Al-RE alloys.

2.1 Thermodynamics and phase diagrams

2.1.1 Fundamentals of phase diagrams

Thermodynamic databases, including phase diagrams, are an essential tool in the optimisation and development of alloys because they aid in saving material and time [1]. Often phase diagrams are referred to as maps in alloy design, because by integrating phase diagrams with the design and development of alloys, prediction of possible precipitating phases, solidification sequences and the relative amounts of secondary phases for the alloys can be made for any given temperature, pressure and composition. This information can significantly improve the control of alloy production.

The important features, such as liquidus and solidus temperatures and phase transitions, can also be determined using phase diagrams. For example, the phase diagram for the binary Mg-Al system, shown in Figure 2.1(a), has a liquidus line separating the liquid from the “liquid + α-Mg” phase field, a solidus line separating the “liquid + α-Mg” from the α-Mg phase field, a solvus line separating α-Mg from a two phase mixture of solid solutions of “α-Mg + β”, and eutectic point, at which a liquid and two solid phases co-exist in equilibrium. The development of microstructure depends on the alloy compositions. For example, the solidification of a hypo-eutectic alloy will have a microstructure evolution as shown in Figure 2.1(b).
Chapter 2 Literature Review

Often it is useful to combine experimental investigations with computational thermodynamics and thermochemistry to understand and predict the solidification behaviour of multi-component alloys (which are often used in commercial alloys), where the complexity increases dramatically with the number of alloying elements [4]. In this case, higher order phase diagrams such as ternary phase diagrams can be practically important. The composition of a ternary alloy can be represented on an equilateral triangle, as shown in Figure 2.2. Each corner represents 100% of an individual element. The temperature contour lines on the liquidus projection can also help to trace the solidification pathway during the cooling process. Further information regarding the fundamentals of phase diagrams can be found elsewhere [5].

Figure 2.1 (a) Equilibrium phase diagram of the Mg-Al binary system [2] and (b) magnification of the lead-tin phase diagram showing microstructure evolution of a hypo-eutectic alloy [3].

Figure 2.2 Liquidus projection for the Mg-Al-Ce system [6].
2.1.2 Equilibrium versus Scheil solidification models

Before considering the solidification models, it is useful to begin this section with the basics of solidification. Solidification processes involve phase transformations, which are related to phase stability under given conditions. In other words, if a phase is unstable at its initial state it will transform into a more stable phase. Gibbs free energy is used to describe the relative stability of a system, in which the total Gibbs energy of a system will reach a minimum when the phases reach equilibrium for a given temperature, composition and pressure. In this case, phase transformations will occur until the system reaches its stable state, which is the minimum Gibbs energy.

In general, there are two simple formulations used to describe the extreme cases of ideal equilibrium and non-equilibrium solidification: the Lever rule and the Scheil-Gulliver model. The equilibrium solidification model assumes that equilibrium is achieved at the solid-liquid interface during growth; it is assumed that growth takes place very slowly so that the solid and liquid phases coexist in thermodynamic equilibrium in the mushy zone (liquid-solid zone) [7]. This assumes that diffusion occurs simultaneously, i.e. there is zero or a negligible amount of resistance for atom transport between solid and liquid phases [8]. For example, when a single crystal of alloy composition, $C_0$, is cooled to a temperature, $T^*$ (which is below the liquidus temperature), the compositions of liquid and solid are $C_{L^*}$ and $C_{s^*}$, respectively, based on the equilibrium (Lever) solidification model [9], as shown in Figure 2.3. The partition coefficient, $K$, is the ratio of the composition of solid and liquid. The ratio indicates the degree of solute segregation. The equilibrium partition ratio can be defined by [9],

$$ K = \frac{C_{s^*}}{C_{L^*}} $$
The value of the equilibrium partition ratio indicates whether an element is partitioning into the liquid (values less than unity), as is the case in a eutectic system, or whether an element is partitioning to the solid dendrite (values greater than unity) [9]. When the partition coefficient is further from unity, the element partitioning is stronger [9]. There are two main physical parameters which contribute to the partition coefficient: the differences in atomic radii (the tendency for an element to be in solid solution) and the chemical potential (the tendency for an element to be in liquid) [9]. The equilibrium solidification model, also known as the Lever rule, is used to describe the composition of the solid phase with respect to the fraction of solid and is given in the equation below [9],

$$C_s = \frac{K \cdot C_0}{(1 - f_s) + K \cdot f_s}$$

Where $C_s$ is the solute concentration in wt.%, $K$ is the partition coefficient, and $f_s$ is the solid fraction. According to the assumption of the equilibrium model, based on complete diffusion in the liquid and solid phases, the final product should have a homogeneous composition, $C_s = C_0$ [8, 9].

In contrast, the Scheil-Gulliver solidification model is based on the assumption that there is no elemental diffusional in the solid, uniform liquid composition, locally equilibrated solid-liquid interfaces and equally dense solid and liquid [10]. Based on this assumption, a consistent increase in rejected solute level in the liquid phase is expected. This segregation continues until
the final liquid region has reached the eutectic composition. The Scheil-Gulliver equation can be described as,

\[ C_s = K \cdot C_0 (1 - f_s)^{K-1} \]

The Scheil-Gulliver equation has been shown to predict the formation of intermetallic phases reasonably well [11]. In addition, the Scheil equation has already been demonstrated to be a good approximation for predicting the microstructure of various casting processes with slow to moderate cooling rates, but extra care should be given for processes that involve high cooling rates such as high pressure die-casting (HPDC) [12].

2.1.3 CALPHAD method

To understand the microstructure evolution of alloys and to obtain useful predictions of the solidification sequence a thermodynamic database is required. It is important that the predictions can provide accurate information on the amount and composition of phases precipitated. This is particularly important for multi-component systems where calculations can be relatively complex. To understand these complex relationships for effective predictions, thermodynamic databases have been developed containing accurate model parameters including intermetallic phases with the associated temperatures and compositions. Only an accurate thermodynamic database will provide effective predictions for alloy selection, and hence be useful in alloy design and optimisation.

CALPHAD is an acronym for the CALculation of PHAse Diagrams. It is also often described as the computer coupling of phase diagrams and thermochemistry [13, 14]. Kaufman and Bernstein [15] began the construction of multicomponent thermodynamic databases and summarised the calculation of phase diagrams as the CALPHAD technique in the 1970s. To date, CALPHAD has been employed to model thermodynamic properties and predict the phase behaviour of many alloy systems [16-19]. Currently, there are multiple thermodynamic software packages using the CALPHAD method, which are also known as integrated computational materials engineering (ICME) tools. These include:

- Thermo-Calc [20]
- MTDATA [21]
- Factsage [22]
- Pandat [23]
These ICME tools have become important for the optimisation and development of alloys. Using this thermodynamic software, the amounts and compositions of all phases at equilibrium at any given temperature and composition in multi-component alloys can be calculated with the choice of equilibrium or non-equilibrium cooling models. Despite the powerful application of thermodynamic prediction tools, it is worth mentioning that a key limitation of these tools remains their inability to indicate the time period required for the attainment of equilibrium [3]. Fortunately, there are other tools available for understanding transient behaviours, such as the diffusion module (DICTRA) in Thermo-Calc [20]. Another key limitation to CALPHAD modelling is the accuracy of the materials database. This is to say that if phases are not in the database, or parameters such as solubility limits or melting temperatures are inaccurate, then the results from these tools will be inaccurate.

In order to understand the formation of solid phases and predict solidification sequences, it is necessary to understand thermodynamic properties and the phase diagrams of alloy systems. Phase diagrams for binary systems are often created based on experimental data. However, experimentally based information for ternary or higher order systems is limited. The CALPHAD method combines thermodynamic information of binary systems to extrapolate ternary or even higher order systems. The enthalpy of formation for a ternary alloy is the sum of enthalpy from the three binary sub-systems [24]. For example, the ternary Mg-Al-RE systems are constructed based on the binary Mg-RE, Mg-Al and Al-RE sub-systems, in which RE is the individual rare earth element in each of the Mg-Al-RE systems. Because most of these ternary systems come from extrapolation of the binary systems, the model parameters in the CALPHAD method can be refined if new experimental data, such as the role and interactions between alloying elements, for the ternary systems become available; this can optimise the thermodynamic description for the ternary systems.

The enthalpy of formation of ternary compounds can be estimated using the model of Miedema [25] as well as via first principles [26]. The Modified Quasichemical Model (MQM) [27-29] is used to model the thermodynamic properties of the liquid phase, whereas the Compound Energy Formalism (CEF) [30-33] is used to describe the Gibbs energy of solid solution phases with sub-lattices. Further information regarding the extension to a ternary system from binary systems can be found elsewhere [13].
2.1.4 The binary Mg-Al system

Since aluminium is one of the most important alloying elements for magnesium and is commonly used in commercial magnesium alloys, the Mg-Al phase diagram and database is considered the most important binary system in magnesium. In this binary system, aluminium has high solubility in magnesium, which gives a magnesium solid solution with maximum solubility of 11.8 at.% at 437 °C.

There have been many studies of the binary Mg-Al phase diagram. For example, the liquidus, solidus and solvus lines in the phase diagram were studied by multiple researchers [34-37], who reported consistent results. In addition, there were studies [38-45] conducted to develop and optimise the thermodynamic description of this system using a combination of the CALPHAD method and experimental techniques. This led to an optimised thermodynamic modelling of the binary Mg-Al system using the available experimental data.

With the experimental data from the past studies, the phases identified in the Mg-Al phase diagram consists of liquid, a β-solid solution (Mg$_{89}$Al$_{140}$) with the hexagonal crystal structure, a γ-solid solution (Mg$_{17}$Al$_{12}$) with an α-Mn structure type, and an ε-solid solution (R phase – Mg$_{23}$Al$_{30}$) with a rhombohedral structure type. Mg$_{89}$Al$_{140}$ has also been reported as a stable phase in the Mg-Al binary system [46]. The maximum composition range of this phase is between 38.5 to 40.3 at.% Mg [47, 48]. Mg$_{23}$Al$_{30}$, also called the R-phase, has a composition of 42 at.% Mg [46]. According to the reported thermodynamic calculations, this phase is only stable between 320 °C and 370 °C [46]. Lastly, Mg$_{17}$Al$_{12}$ has a wider single-phase field from 45 to 60.5 at.% Mg at 450 °C, and a narrower phase field from 52 to 60 at.% Mg at 300 °C [46]. The crystallographic data for the intermetallic phases in this system are listed in Table 2.2. The calculated Mg-Al phase diagram is shown in Figure 2.5.

Table 2.1 Crystal structures for Mg-Al intermetallic phases.

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Space Group</th>
<th>Lattice Parameters (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$<em>{23}$Al$</em>{30}$ (ε)</td>
<td>R3h</td>
<td>1.2825 2.1748</td>
<td>[49]</td>
</tr>
<tr>
<td>Mg$<em>{89}$Al$</em>{140}$ (β)</td>
<td>Fd3m</td>
<td>2.8300</td>
<td>[49]</td>
</tr>
<tr>
<td>Mg$<em>{17}$Al$</em>{12}$ (γ)</td>
<td>I43m</td>
<td>1.0544</td>
<td>[49]</td>
</tr>
</tbody>
</table>
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2.1.5 The binary Mg-RE systems

The Mg-Ce phase diagram in the composition range of 18 to 100 at.% Ce was first reported by [51], and then revised by [52]. The Mg-rich end of the phase diagram was also studied by [53-57]. Based on the previous studies, the intermetallic phases, Mg$_3$Ce, forms from the liquid [51]. Whereas, MgCe, Mg$_2$Ce, Mg$_{41}$Ce$_5$, Mg$_{12}$Ce, Mg$_{10.3}$Ce and Mg$_{17}$Ce$_2$ form through peritectic reactions in the Mg-rich corner of this binary system [56, 58, 59]. In addition, Mg$_{12}$Ce is found to be a stable phase in the Mg-Ce system [11]. The calculated Mg-Ce phase diagram is shown in Figure 2.5. The crystallographic data for the intermetallic phases in this system are listed in Table 2.2.

Figure 2.4 Equilibrium phase diagram of the Mg–Al binary system [50].

![Figure 2.4](image1)

Figure 2.5 Equilibrium phase diagram of the Mg–Ce binary system [50].

![Figure 2.5](image2)
The binary Mg-La system was first determined by [61], and then revised by [52, 62-65]. This binary system consists of liquid, Mg solid solution, α-La, β-La and γ-La solid-solution, Mg_{12}La, Mg_{17}La₂, Mg₃La, Mg₅La and MgLa [66]. The Mg_{12}La, Mg₃La and MgLa phases have homogeneity ranges in the phase diagram [66]. Similar to the binary Mg-Ce system, Mg₃La is formed from the liquid [52], whereas other intermetallic phases in this system are formed peritectically [66]. The Mg_{12}La phase is also found to be a stable phase in the Mg-La system [11]. The intermetallic phases in the binary Mg-Ce phase diagram were used as a reference for the development of this binary Mg-La system. For example, it was reported that the Mg_{17}La₂ is expected to form through a peritectic reaction at 672 °C in this system based on the homologous Mg-Ce phase diagram [66]. The calculated Mg-La phase diagram is shown in Figure 2.6. The crystallographic data for the intermetallic phases in this system are listed in Table 2.3.
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Figure 2.6 Equilibrium phase diagram of the Mg–La binary system [66].

Table 2.3 Crystal structures for Mg-La intermetallic phases [66].

<table>
<thead>
<tr>
<th>Phase name</th>
<th>Space Group</th>
<th>Lattice Parameters (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(γ-La)</td>
<td>Im3m</td>
<td>0.4260</td>
<td>[67, 68]</td>
</tr>
<tr>
<td>(β-La)</td>
<td>Fm3m</td>
<td>0.5303</td>
<td>[67, 68]</td>
</tr>
<tr>
<td>(α-La)</td>
<td>P63/mmc</td>
<td>0.3774 1.2171</td>
<td>[67, 68]</td>
</tr>
<tr>
<td>Mg₁₂La</td>
<td>Immm</td>
<td>1.0336 7.7560</td>
<td>[69]</td>
</tr>
<tr>
<td>Mg₁₇La₂</td>
<td>P63/mmc</td>
<td>1.0350 1.0250</td>
<td>[69]</td>
</tr>
<tr>
<td>Mg₁₃La</td>
<td>Fm3m</td>
<td>0.7467</td>
<td>[70]</td>
</tr>
<tr>
<td>Mg₂La</td>
<td>Fd3m</td>
<td>0.8801</td>
<td>[71]</td>
</tr>
<tr>
<td>MgLa</td>
<td>Pm3m</td>
<td>0.3962</td>
<td>[72]</td>
</tr>
<tr>
<td>Mg</td>
<td>P63/mmc</td>
<td>0.3209 0.5211</td>
<td>[49, 66]</td>
</tr>
</tbody>
</table>

The binary Mg-RE phase diagrams suggest that the different rare earths can behave differently, i.e. the binary Mg-Ce and Mg-La systems have some notable differences. It is found that there are systematic changes observed between the characteristics of the phase diagram and the atomic number of the rare earth elements [11, 73] (Table 2.4). In the binary Mg-La phase diagram, lanthanum has the lowest solid solubility (C<sub>ss</sub>), but the highest eutectic temperature (T<sub>eut</sub>) and the lowest eutectic composition (C<sub>eut</sub>). Compared to lanthanum, neodymium (Mg-Nd phase diagram) has the highest solid solubility, but the lowest eutectic temperature and the
highest eutectic composition. Lastly, as for cerium (Mg-Ce phase diagram), it is located somewhere in between, but closer to the lanthanum side [11].

Table 2.4 The important features obtained from the Mg-RE binary phase diagrams [11, 74, 75].

<table>
<thead>
<tr>
<th>Rare earth no.</th>
<th>Atomic no.</th>
<th>Maximum solid solubility, $c_{cs}$ (wt.% RE)</th>
<th>Eutectic composition, $c_{eut}$ (wt.% RE)</th>
<th>Eutectic temperature, $T_{eut}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La</td>
<td>57</td>
<td>0.23</td>
<td>16.5*</td>
<td>612</td>
</tr>
<tr>
<td>Ce</td>
<td>58</td>
<td>0.74</td>
<td>20.5</td>
<td>590</td>
</tr>
<tr>
<td>Nd</td>
<td>60</td>
<td>3.6</td>
<td>33</td>
<td>552</td>
</tr>
</tbody>
</table>

2.1.6 The binary Al-RE systems

Like the previous binary systems, the Al-Ce and Al-La binary systems have been studied and reviewed using both experimental and thermodynamic investigations [28, 76-84]. The binary Al-Ce phase equilibria was first investigated by Vogel [85] and then followed by Van Vucht [86]. Buschow and Van Vucht [76] also investigated in the whole composition range of this system. Kononenko and Golubev [87] focused on the Al-rich region of the Al-Ce system with up to 3 at.% Ce. On the other hand, Saccone et al. [77] studied within the Ce-rich region of this system with up to 35 at.% Al. The data from these studies were also reviewed and optimised by [78, 79, 82]. This system was also thermodynamically studied by [88-91]. In the binary Al-Ce system, there are eight Al-Ce intermetallic phases: $\alpha$-$\text{Al}_{11}\text{Ce}_3$, $\beta$-$\text{Al}_{11}\text{Ce}_3$ (also called $\text{Al}_4\text{Ce}$), $\text{Al}_3\text{Ce}$, $\text{Al}_2\text{Ce}$, $\text{AlCe}$, $\alpha$-$\text{AlCe}_3$, and $\beta$-$\text{AlCe}_3$, and $\text{AlCe}_2$ [79, 82]. The binary Al-Ce phase diagram is shown in Figure 2.7(a), and a summary of all Al-Ce intermetallic phases and their associated crystallographic information are presented in Table 2.5.
Figure 2.7 (a) Al-Ce phase diagram from [78] compared with a selection of experimental points from [76, 77, 92, 93], and (b) Al-La phase diagram from [78] compared with a selection of experimental points from [77, 93, 94].

<table>
<thead>
<tr>
<th>Al-Ce</th>
<th>Space Group</th>
<th>Lattice Parameters (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>$Fm\overline{3}m$</td>
<td>0.4050</td>
<td>[49]</td>
</tr>
<tr>
<td>($\delta$-Ce)</td>
<td>$Fm\overline{3}m$</td>
<td>0.4821</td>
<td>[49]</td>
</tr>
<tr>
<td>($\gamma$-Ce)</td>
<td>$Im\overline{3}m$</td>
<td>0.4120</td>
<td>[49]</td>
</tr>
<tr>
<td>Al$_2$Ce</td>
<td>$Fd\overline{3}m$</td>
<td>0.7700</td>
<td>[49]</td>
</tr>
<tr>
<td>$\alpha$-Al$_{11}$Ce$_3$</td>
<td>$I4/mmm$</td>
<td>0.4395 1.3025 1.0092</td>
<td>[49]</td>
</tr>
<tr>
<td>$\beta$-Al$_{11}$Ce$_3$</td>
<td>$I4/mmm$</td>
<td>0.4539 1.1160</td>
<td>[49]</td>
</tr>
<tr>
<td>Al$_3$Ce</td>
<td>$P6_3/mmc$</td>
<td>0.6541 0.4610</td>
<td>[49]</td>
</tr>
<tr>
<td>AlCe</td>
<td>$Cmcm$</td>
<td>0.9270 0.7680 0.5760</td>
<td>[49]</td>
</tr>
<tr>
<td>$\alpha$-AlCe$_3$</td>
<td>$P6_3/mmc$</td>
<td>0.7043 0.5451</td>
<td>[49]</td>
</tr>
<tr>
<td>$\beta$-AlCe$_3$</td>
<td>$Pm\overline{3}m$</td>
<td>0.4985</td>
<td>[49]</td>
</tr>
</tbody>
</table>

The binary Al-La phase equilibria have been seldom investigated compared to the Al-Ce binary system. This system is mainly investigated by Buschow [94] over the whole composition range. Kononenko and Golubev [87] investigated the Al-rich region of this system with up to 3 at.% La. On the other hand, Saccone et al. [77] focused on the La-rich region of this system with up to 35 at.% Al. The data for this binary system was then reviewed and compiled by Gschneidner and Calderwood [80]. In addition, there are also studies focused on the thermodynamics of the Al-La intermetallic phases. Thermodynamic optimisation of this system was performed by
Wang [95]. Following on from this, Zhao et al. [83] optimised the phase diagram using a combination of thermodynamic and first-principles approaches. The study reported that the Gibbs free energy versus composition curves for all Al-La phases were estimated. The associated phase diagram was also reported, which shows several key differences from the previously reported phase diagrams. The binary Al-La phase diagram is shown in Figure 2.7(b).

A summary of the currently discovered Al-La intermetallic phases and their associated crystallographic information are also presented in Table 2.6.

<table>
<thead>
<tr>
<th>Al-La</th>
<th>Space Group</th>
<th>Lattice Parameters (nm)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(β-La)</td>
<td>$Fm\bar{3}m$</td>
<td>a: 0.5170 b:</td>
<td>[49]</td>
</tr>
<tr>
<td>(γ-La)</td>
<td>$Im\bar{3}m$</td>
<td>c: 0.4260</td>
<td>[49]</td>
</tr>
<tr>
<td>(α-La)</td>
<td>$P6_3/mmc$</td>
<td>b: 0.3770 c: 1.2159</td>
<td>[49]</td>
</tr>
<tr>
<td>Al$_3$La</td>
<td>$Fd\bar{3}m$</td>
<td>c: 0.8149</td>
<td>[49]</td>
</tr>
<tr>
<td>α-Al$_{11}$La$_3$</td>
<td>$I4/mmm$</td>
<td>a: 0.4431 b: 1.3142 c: 1.0132</td>
<td>[49]</td>
</tr>
<tr>
<td>β-Al$_{11}$La$_3$</td>
<td>$I4/mmm$</td>
<td>a: 0.4539 b: 1.1160</td>
<td>[49]</td>
</tr>
<tr>
<td>Al$_3$La</td>
<td>$P6_3/mmc$</td>
<td>a: 0.6667 c: 0.3461</td>
<td>[49]</td>
</tr>
<tr>
<td>Al$<em>{53}$La$</em>{22}$</td>
<td>$P6_3/mmc$</td>
<td>a: 0.4478 c: 0.4347</td>
<td>[49]</td>
</tr>
<tr>
<td>AlLa</td>
<td>$Cmcm$</td>
<td>a: 0.9531 c: 0.7734</td>
<td>[49]</td>
</tr>
<tr>
<td>AlLa$_3$</td>
<td>$P6_3/mmc$</td>
<td>a: 0.7192 c: 0.5528</td>
<td>[49]</td>
</tr>
</tbody>
</table>

Comparing the two binary Al-Ce and Al-La systems, Al$_{53}$La$_{22}$ (also known as Al$_5$La$_2$) phase is reported in the Al-La phase diagram but there is no similar phase in the binary Al-Ce system. Whether a similar phase exists in the Al-Ce alloys is yet to be investigated.

### 2.1.7 The ternary Mg-Al-RE systems

Compared with the binary systems outlined in Sections 2.1.4 to 2.1.6, the ternary Mg-Al-RE systems are more complex due to multi-component interactions. There have been relatively few experimental investigations of the Mg-Al-RE systems. As a result, the current ternary phase diagrams for Mg-Al-RE alloys are based largely on extrapolations from the relevant binary systems. Figure 2.8 shows the liquidus projections for Mg-Al-Ce and Mg-Al-La generated by Pandat® using the PanMagnesium 2018 database [96]. From these projections it
can be seen that the melting temperature varies as a function of alloy composition (highlighted by the contour lines) and the primary solid phases are all calculated to be binary compounds.

![Figure 2.8 Liquidus projection of the ternary (a) Mg-Al-Ce system and (b) Mg-Al-La system [96].](image)

The evaluation and optimisation of the thermodynamic descriptions for the binary Mg-RE, Mg-Al and Al-RE sub-systems as mentioned previously are useful for the development of the Mg-Al-RE phase diagrams, which come from the magnesium alloy thermodynamic database with 21 components determined by [97]. Each of the binary intermetallic phases was investigated thermodynamically and their crystal structures have been studied in detail [97]. The Al-Mg-La and Al-Mg-Ce ternary systems were also optimised independently by Hosseinifar and Malakhov [98] and Grobner et al. [99], respectively.

For the Mg-Al-Ce system, two ternary phases, Al$_{23}$CeMg$_9$ and Al$_4$CeMg$_4$, have been reported [100], but their crystal structures were not characterised and these ternary phases have not been
observed in later studies. In addition, a ternary phase, Al$_{67}$Ce$_5$Mg$_{28}$, was identified with a MgZn$_2$ type structure in a study that was focused on the isothermal section at (400 °C) 673 K for Ce compositions up to 33.3 at.% [101]. When the binary systems are combined into the ternary system, Mg$_2$Ce and Al$_2$Ce have a continuous solid solution with a miscibility gap of 5-20 at.% Mg [102]. A similar observation was reported for MgCe and AlCe with a solid solution up to approximately 30 at.% Al [102].

In the experimental work by Odinaev et al. [103], the thermal analysis revealed very low liquidus temperatures in the Al-Ce-Mg system. Other researchers [99], however, who have compared thermodynamic data and experimental work, have found that the liquidus temperatures for the ternary Al-Ce-Mg system are higher. The higher liquidus temperatures for alloys in this system can be explained by the high enthalpies of formation and normal entropies of the binary Al-Ce phases, such as Al$_{11}$Ce$_3$ and Al$_2$Ce. Table 2.7 provides a comparison between the liquidus and solidus temperatures of the ternary Mg-Al-Ce system determined by experimental methods and calculated using Scheil predictions. The inconsistencies between experimental observations and the calculated phase diagrams for multiple systems have motivated several studies [17, 104].

Table 2.7 Comparison between the liquidus and solidus temperatures determined by experimental observations and Scheil calculations [6].

<table>
<thead>
<tr>
<th></th>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Liquidus</td>
<td>Solidus</td>
</tr>
<tr>
<td>Mg - 4 Al - 4 Ca</td>
<td>604</td>
<td>509</td>
</tr>
<tr>
<td>Mg - 4 Al - 4 Sr</td>
<td>615</td>
<td>550</td>
</tr>
<tr>
<td>Mg - 4 Al - 4 Ce</td>
<td>629</td>
<td>605</td>
</tr>
<tr>
<td>Mg - 4 Al - 4 La</td>
<td>629</td>
<td>604</td>
</tr>
<tr>
<td>Mg - 4 Al - 2 Ca</td>
<td>620</td>
<td>520</td>
</tr>
<tr>
<td>Mg - 4 Al - 2 Sr</td>
<td>629</td>
<td>537</td>
</tr>
<tr>
<td>Mg - 4 Al - 2 Ce</td>
<td>631</td>
<td>605</td>
</tr>
<tr>
<td>Mg - 4 Al - 2 La</td>
<td>631</td>
<td>602</td>
</tr>
</tbody>
</table>

The eutectic temperatures for the Al$_{11}$Ce$_3$, Al$_2$Ce and Mg$_{12}$Ce phases can also be calculated from the Mg-Al-Ce ternary phase diagram using the Scheil-Gulliver equation to be 560 °C, 622
°C and 867 °C, respectively [105, 106]. Compared to Mg$_{17}$Al$_{12}$, which has a eutectic at 436 °C, the eutectic temperatures of the former three phases are significantly higher.

In the Mg-Al-La system, Raghavan [107, 108] reviewed the 400 °C isothermal section of the phase diagrams, and showed that there is a ternary compound with the formula Al$_2$Mg$_{0.85}$La$_{0.15}$, denoted as the τ phase. This phase was later identified to have a MgZn$_2$ type crystal structure [102]. This phase is most likely similar to the Al$_{67}$Ce$_5$Mg$_{28}$ compound reported in the Mg-Al-Ce system [109]. On the other hand, although Mg$_{12}$La is in the optimised Mg-La system [107], the existence of the Mg$_{12}$La phase remains the subject of some debate [110, 111]. When it comes to solubility in this system, the solubility of Al in Mg$_{17}$La$_2$ and Mg$_3$La is reported to be minimal [107, 112]. Whereas, similar to the ternary Mg-Al-Ce system, there is an extensive solid solution between Mg$_2$La and Al$_2$La with a miscibility gap of 20-37 at.% Mg, as well as between MgLa and AlLa with approximately 19 at.% Al [102]. In the experimental work by Odinaev et al. [102], the liquidus temperatures for the ternary Mg-Al-La system were determined. This was also further verified by Hosseinifar and Malakhov [98].

Despite the work on ternary Mg-Al-RE systems, a previous study indicates that it is inadequate to apply only binary system descriptions to ternary or higher magnesium alloy applications [97], because thermodynamic descriptions of the intermetallic solid solution should not be based solely on the binary systems but also extended to the ternary system. In addition, there are inconsistent liquidus temperatures reported in the literature for both the Mg-Al-Ce and Mg-Al-La systems [98, 102, 109, 113]. There is also varying liquidus lines for Al$_2$Ce and Al$_{11}$Ce$_3$ reported in different studies [102, 113]. Therefore, these results suggest further investigations are needed to develop comprehensive thermodynamic databases for Mg-Al-RE ternary systems to achieve accurate predictions for alloy design.

### 2.2 Solidification and microstructure development in Mg-Al-RE alloys

Solidification and its resultant microstructure are fundamental to the alloy development process. This is because solidification processes influence the formation of microstructure and hence the mechanical properties of alloys. In other words, the final microstructure and mechanical properties of a cast alloy are highly dependent on the nucleation and subsequent growth of the primary phase, the intermetallic phases and the eutectic phases [114, 115]. The morphology, such as the size and shape, of the primary phase influences how the subsequent eutectic morphology forms upon solidification [114].
This section focuses on the solidification and microstructure development in the binary Mg-Al, Mg-RE and Al-RE sub-systems, as well as the ternary Mg-Al-RE systems. Microstructural characterisations of these systems are discussed in this section.

### 2.2.1 The binary Mg-Al system

A good understanding of the solidification behaviour and microstructure in Mg-Al alloys is important given that the majority of commercial magnesium alloys are based on Mg-Al alloys. For this reason, there has been a considerable amount of work on Mg-Al alloys [11, 116-119]. The growth morphologies of the phases in the Mg-Al system have been shown to be highly dependent on the aluminium alloying content [115, 120]. One of the reasons is that aluminium has a high solubility in magnesium, which is approximately 12 wt.% at the eutectic temperature [11, 116, 121, 122].

In Mg-Al based alloys, the most commonly reported phases are α-Mg and Mg$_{17}$Al$_{12}$, which often form as part of the eutectic phase in low aluminium content alloys. This can also be seen from the binary Mg-Al phase diagram, as mentioned in Section 2.1.4 (Figure 2.4). Aluminium in Mg-Al based alloys can dissolve in the α-Mg phase forming a solid solution, but also can contribute to forming Mg$_{17}$Al$_{12}$ in the eutectic [2], which is mainly located at the grain boundaries, as shown in Figure 2.9(a). The eutectic phase increases as the aluminium content increases towards the solubility limit. Once it reaches 44 wt.% Al, the Mg-44Al alloy mainly consists of the Mg$_{17}$Al$_{12}$ intermetallic phase only [2], as shown in Figure 2.9(b). Another study [123] also reported the α-Mg phase with a fully divorced eutectic α-Mg + Mg$_{17}$Al$_{12}$ phase in HPDC AM50 (Mg-5Al-0.4Mn) alloy. There is also a Al$_8$Mn$_5$ phase with a polygonal microstructure observed in this alloy [123], which is common for Mg-Al alloys that contain some Mn.
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Figure 2.9 Solidified microstructure of (a) the Mg-4Al alloy [2] with the primary α-Mg appearing as the darker part, and the Mg\(_{17}\)Al\(_{12}\) (labelled as β) eutectic phase appears brighter, and (b) the Mg-44Al alloy [124] with the white phase being the Mg\(_{17}\)Al\(_{12}\) intermetallic.

The eutectic structure in Mg-Al based alloys is correlated with the aluminium concentration in the alloy [114]. For example, in most commercial die-casting magnesium alloys, it is found that eutectic structures are generally developed in the form of fully or partially divorced eutectic due to the low content of aluminium (Figure 2.10(c) and (d)), which is generally not more than 9 wt.% Al. When the aluminium content increases to more than 12 wt.%, the eutectic structure starts to develop and form lamellar or fibrous morphologies (Figure 2.10(a) and (b)). For the commercial die-casting Mg-Al alloys (often low Al content), the fully divorced eutectic is more commonly observed due to the high cooling conditions in die-casting. Whereas, partially divorced eutectic is anticipated during lower cooling rates [114].

Figure 2.10 The eutectic (α-Mg + Mg\(_{17}\)Al\(_{12}\)) is (a) a lamellar or (b) a fibrous morphology when the aluminium content is more than 12 wt.% in Mg-Al based alloys, whereas the eutectic structure has (c) partially divorced or (d) fully divorced morphologies when the aluminium content decreases to less than 9 wt.% [114, 120, 125].

54
In one study [2], the solidification path for Mg-4Al (Figure 2.11) was also simulated and compared with their experimental observations. According to the Scheil-Gulliver description of the solidification path, as shown in Figure 2.11, the phase formation sequence is,

\[
\text{Liquid} \rightarrow \text{Liquid} + \alpha(Mg) \rightarrow \text{Liquid} + \alpha(Mg) + \beta(Mg_{17}Al_{12})
\]

The Scheil-Gulliver model predicts that the primary phase developed is $\alpha$-Mg, followed by a eutectic structure of $\alpha$-Mg and $Mg_{17}Al_{12}$ at the final stage of solidification [2]. This agrees with their microstructural observation.

2.2.2 The binary Mg-RE systems

In Mg-RE alloys, the intermetallic phases and the associated microstructure can be very different depending on the individual RE alloying element. For example, $Mg_{12}Ce$ and $Mg_{12}La$ intermetallic phases were identified in Mg-Ce and Mg-La alloys, whereas $Mg_3Nd$ was found in Mg-Nd alloys [11]. The findings of this study also show that the $Mg_{12}La$ and $Mg_3Nd$ phases in Mg-La and Mg-Nd alloys have a lamellar eutectic structure, but that $Mg_{12}Ce$ in Mg-Ce alloys appears to be a rod-shaped phase within the intermetallic matrix. The reason for the different morphology of these phases depends on the proportion of phases based on the phase diagram, and the authors [11] suggest that further study is necessary in order to understand the mechanism of this phenomenon.
In the same study [11], the amount of intermetallics and $\alpha$-Mg within the eutectic phase were calculated. Table 2.8 shows that the Mg-Ce alloys contain Mg$_{12}$Ce, which has the highest volume fraction of intermetallic while Mg-Nd alloys contain Mg$_3$Nd has the smallest volume fraction of intermetallic among the three alloys investigated. In addition, the amount of intermetallic phase in the eutectic is reported to influence the eutectic morphology. For example, a rod-like morphology is likely to form if the volume fraction of a minor phase is less than 32 %, whereas a lamellar morphology is likely to form when the volume fraction of a minor phase is more than 32 % [8].

Table 2.8 Volume fraction of the intermetallic phase and $\alpha$-Mg within the eutectic phase, estimated using maximum solid solubility from the phase diagrams [11].

<table>
<thead>
<tr>
<th>Intermetallic phase</th>
<th>Mg$_{12}$Ce</th>
<th>Mg$_{12}$La</th>
<th>Mg$_3$Nd</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$-Mg (vol.%)</td>
<td>44.16</td>
<td>55.81</td>
<td>69.93</td>
</tr>
<tr>
<td>Intermetallic (vol.%)</td>
<td>55.84</td>
<td>44.19</td>
<td>30.07</td>
</tr>
</tbody>
</table>

As the RE concentration increases in the alloys, the amount of intermetallic or eutectic also increases [11], as shown in Figure 2.13. In addition, the nucleation rate increases and the grain
size reduces when the RE content increases in Mg-RE alloys [11]. These results are reported to be qualitatively matched with grain refinement theory, which suggests that solute additions can help to increase nucleation and restrict grain growth [11, 126, 127].

From the literature and phase diagrams (Section 2.1.5), it can be seen that alloys in this binary system can have many possible intermetallic phases, many of which are common to several different rare earth elements, such as Mg\textsubscript{12}RE, Mg\textsubscript{17}RE\textsubscript{2}, Mg\textsubscript{3}RE, or Mg\textsubscript{2}RE phases [11, 74]. Although there is a considerable amount of research on Mg-RE alloys, very little was found in the literature on the question of what phases will nucleate and form under given solidification conditions. For example, there is a debate about the formation of Mg\textsubscript{12}La as opposed to Mg\textsubscript{17}La\textsubscript{2} in the Mg-La system [11, 74, 75, 128]. A previous study [129] also shows that different metastable phases develop based on the cooling rate. The study conducted on Mg-Nd alloys identified that Mg\textsubscript{12}Nd forms at slow solidification rates and Mg\textsubscript{3}Nd forms at fast cooling rates. Another phase, Mg\textsubscript{41}Nd\textsubscript{5}, only forms at high heat treatment temperature and when sufficient cooling time is allowed.
2.2.3 The binary Al-RE systems

Compared to the binary Mg-Al and Mg-RE systems, there is relatively limited information in the literature on the solidification and microstructure development in the Al-RE system. Al₁₁RE₃ is a commonly reported phase in the binary Al-RE (and ternary Mg-Al-RE) systems. In the literature, the microstructure evolution of die-cast Al-La alloys was investigated using XRD, SEM and EDS by He et al. [130]. These authors investigated three alloys, Al-10La, Al-15La and Al-20La, all of which consisted of α-Al and Al₁₁La₃, in agreement with the binary Al-La phase diagram [95]. The Al-10La alloy is reported to be a hypo-eutectic alloy, whereas the Al-15La and Al-20La alloys are hyper-eutectic. Figure 2.14 shows that the Al-10La alloy mainly consists of α-Al + Al₁₁La₃ eutectic phase with a minimal amount of primary α-Al phase because the α-Al phase field in the phase diagram is very narrow (Figure 2.7(b)). In the Al-15La alloy, there is an additional laminar shaped primary Al₁₁La₃ phase. Lastly, the Al-20La alloy shows a particle shaped primary Al₁₁La₃ phase.

![Figure 2.14 As-cast microstructure of (a) Al-10La, (b) Al-15La and (c) Al-20La alloys [130].](image)

In other studies [131, 132], it is interesting that the dendrites in an Al-35La alloy are composed of two phases, α-Al and Al₁₁La₃ (Figure 2.15). The proposed description of these dendrites is that the alternate nucleation of α-Al and Al₁₁La₃ results in the formation of a periodic diphasic dendrite structure (Figure 2.16). This finding is very different from the typical tree-like dendrite, which is commonly composed of a single phase.
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2.2.4 The ternary Mg-Al-RE systems

In ternary Mg-Al-RE systems, Al$_{11}$RE$_3$ and Al$_2$RE are the commonly reported phases in commercial magnesium alloys, such as AE44 [133-143]. Al$_{11}$RE$_3$, which has a needle-like microstructure, is commonly reported as the dominant intermetallic phase in AE44 [144-149]. Whereas, Al$_2$RE has a particulate-like structure and is often reported as the minor intermetallic phase in AE44 [144, 146, 147, 149]. Interestingly, Khan et al. [9] claim that the dominant intermetallic phase developed in the AE44 alloy is Al$_{11}$RE$_3$, and a small amount of Al$_3$RE rather than Al$_2$RE. Another investigation [150] shows that the microstructure of AE44 is characterised by α-Mg solid solution (point “4”), polyhedral Al$_3$RE (point “1”), acicular-like Al$_{11}$RE$_3$ (point “2”) and blocky precipitates of the Al$_6$CeMn$_4$ phase (point “3”) in the ingot before die-casting, as shown in Figure 2.17(a). However, the microstructure of AE44 changes after hot chamber die-casting. Using EDS analysis, the microstructure transforms to equiaxed...
dendrites of α-Mg (point “1”) with precipitates of Al$_{11}$RE$_3$ (point “3”) and probably the Al$_2$RE phase (point “2”), as shown in Figure 2.17(b). This may explain the presence of Al$_2$RE and Al$_3$RE phases in the alloys, as being dependent on the casting conditions.

The study by Wei et al. [151] reveals the interdendritic phases of Al$_4$RE and Mg$_{17}$Al$_{12}$ formed in AE41 and AE91, but only Al$_4$RE appears in AE21, using qualitative microscopy analysis and quantitative energy dispersive X-Ray (EDX) approaches. The Al$_4$RE phase is observed to precipitate concurrently with α-Mg dendrites. There is no ternary Mg-Al-RE phase found and no Al$_2$RE/Al$_3$RE phase observed in these low RE content alloys. This observation of the phases present is in line with the findings of Pettersen et al. [145]. In addition, it is commonly reported that RE addition to Mg-Al based alloys leads to the preferential formation of Al-RE intermetallic phases and hence suppresses the Mg$_{17}$Al$_{12}$ phase [138, 152, 153]. Apart from the preferential intermetallic formation, Sun et al. [12] also reported that the supersaturation of aluminium in magnesium can leads to the suppression of Mg$_{17}$Al$_{12}$. However, some studies reported the presence of Mg$_{17}$Al$_{12}$ in the ternary AE alloys, while other studies show that no Mg$_{17}$Al$_{12}$ was found in the structure of Mg-Al-RE alloys when the ratio of Al/RE is greater than 0.5 during solidification at the cooling rates of HPDC [139].

It is noted that the Al$_{11}$RE$_3$ phase reported in the literature can also sometimes be called the Al$_4$RE. Later investigations based on thermodynamic stability calculations using first-principles, such as density functional theory (DFT) [154] and the quasi-harmonic approach [155], show that this needle-like phase should be correctly known as Al$_{11}$La$_3$, not Al$_4$La. Likewise, Al$_4$RE and Al$_4$Ce should also be known as Al$_{11}$RE$_3$ and Al$_{11}$Ce$_3$, respectively, due to their interchangeable crystal structure [154, 155].
Besides the inconsistency observed in the formation of Al₃RE and Al₂RE, investigations have also shown that there is an inconsistency in which intermetallic phase is dominant in AE alloys. Khan et al. [9] and Zhu et al. [141] claim that the lamellar-like Al₁₁RE₃ phase is the dominant phase. This is also supported by the findings of Bai et al. [156] and Zhang et al. [138]. However, this contradicts what was reported previously by Bakke and Westengen [157], who mention that Al₂RE is the predominant intermetallic phase in AE44. In addition, the AE44 alloy patented by Hydro Magnesium contains Al₂RE as the dominant phase as well, whereas other alloys such as ACe44 has Al₁₁Ce₃ as the dominant phase, possibly with a minority of Al₃Ce intermetallic [158].

There has also been a debate on whether the Al₁₁RE₃ phase decomposes into other phases. Thermodynamic stability calculations using first-principles theory with the quasi-harmonic approach indicate that the Al₁₁La₃ phase does not decompose into Al₂La under aging [155]. This also agrees with the experimental results of Zhu et al. [147] who found that Al₁₁RE₃ and Al₂RE in die-cast AE42 appear to have high thermal stability without any decomposition observed during aging at temperatures up to 200 °C. However, others have reported that Al₁₁RE₃ decomposes into Al₂RE on heating [144, 148, 158-161]. For example, Rzychon et al. [139] observed a change in the morphology of Al₁₁RE₃ precipitates from needle-like to spheroid shape after annealing at 250 °C. Another study [162] claims that the instability of the Al₁₁RE₃ phase is because of the presence of cerium in its crystal structure. They show that the Al₁₁La₃ phase does not transform when the temperature is held at 175 °C for 1200 hours, whereas the Al₁₁RE₃ phase tends to transform into Al₂RE when held at the same condition. In a separate study [133], Al₂Ce and Al₂RE are also present when cerium is used, but not in an alloy system containing only lanthanum as the rare earth element, as shown in Figure 2.18. These studies are in line with a previous study [163], which claims that the individual rare earth element significantly affects the thermal stability of Al₁₁RE₃. Powell et al. [144] and Zhu et al. [147], also claim that the absence of Al₂La in Mg-Al-La alloys is because of the preferential segregation of lanthanum into Al₁₁La₃.
Some researchers claim that thermal stability is also subject to annealing temperatures and the RE/Al ratio [158, 159]. These studies indicate that the RE/Al ratio can have a significant role in phase stabilisation; by varying the RE/Al ratio in the alloys, Al\textsubscript{11}RE\textsubscript{3} and Al\textsubscript{2}RE can be replaced by Al\textsubscript{2}RE phase [158]. In addition, some studies [137, 144, 164] show that Al\textsubscript{2}RE formation is favoured at slow cooling rates through sand and permanent mould casting, whereas the Al\textsubscript{4}RE/Al\textsubscript{11}RE\textsubscript{3} phase is found at high cooling rates through high pressure die-casting. Despite the numerous studies that have attempted to explain this phenomenon, it remains unclear whether Al\textsubscript{11}RE\textsubscript{3} is stable or will decompose into Al\textsubscript{2}RE during aging. Even if it decomposes into another phase as observed in some of these studies, the discrepancy in the decomposition behaviour could be attributed to various factors, such as the individual RE constituents, preferential segregation, RE/Al ratio, annealing and cooling temperatures.

Previous research into the morphology of rare earth-containing intermetallic phases has also been inconsistent and contradictory [9, 133, 140, 165-167]. The morphology of Al\textsubscript{11}RE\textsubscript{3} is often identified as acicular-like and Al\textsubscript{2}RE is quadrate-like or polyhedral in shape [133, 140, 165, 167]. Tian et al. [166] claim that the Al\textsubscript{3}RE phase has an acicular-like morphology (Figure

\textit{Figure 2.18} Backscatter electron micrographs of (a) Mg-4Al-4La-0.4Mn containing Al\textsubscript{11}La\textsubscript{3}, (b) Mg-4Al-4La/Ce-0.4Mn containing Al\textsubscript{11}RE\textsubscript{3} and Al\textsubscript{2}RE, and (c) Mg-4Al-4Ce-0.4Mn containing Al\textsubscript{11}Ce\textsubscript{3} and Al\textsubscript{2}Ce [133].
2.19(a)), yet a recent investigation [9] provides conflicting evidence and has shown that the morphology of Al\textsubscript{3}RE is particulate or globular in shape, as highlighted in Figure 2.19(b). The Al\textsubscript{11}RE\textsubscript{3} and Al\textsubscript{2}RE are found along the grain boundaries in the AE44 alloy [133, 134].

![Figure 2.19 SEM micrographs of the as-cast (a) as-cast Mg-3Al-2Y-1Ce alloy [166] and (b) AE44 [9].](image)

On the other hand, previous studies [149, 168] also show that the morphology of the eutectic can be affected by ternary alloying concentrations. For example, Gavras et al. [168] identified that the eutectic morphology at ternary alloying additions of equal to or less than 1.0 wt.% was lamellar and the morphology transforms into a divorced eutectic at higher ternary concentrations. In addition, dendrite arm spacing is shown to be larger with reduced cerium content in the Mg-Al-Ce system, as shown in Figure 2.20.

![Figure 2.20 Effect of cerium content on the dendrite arm spacing (DAS) of HPDC Mg-Al-Ce alloys [149].](image)
To summarise, a number of Al-RE intermetallic phases have been observed in Mg-Al-RE alloys and it appears that rare earths react with aluminium only; there is no formation of Mg-RE and Mg-RE-Al phases in the low RE-content alloys [145]. However, rare earths can form intermetallic with magnesium and form either a binary Mg-RE intermetallic in the binary system or a ternary intermetallic phase. Aluminium and rare earths are generally formed as Al-RE intermetallic phases with the assumption of no magnesium solubility and all rare earths in the alloy are consumed completely to react with aluminium only. In the Mg-Al-RE alloys with high RE concentration, the extra rare earth that has not been consumed by aluminium can react with magnesium (with limited solubility), which means the solidification path can move towards the binary Mg-RE region in the phase diagram. There remains limited experimental data in the literature on the high RE content alloys.

The review of the literature reveals inconsistencies in which phases are reported to form in the Mg-Al-RE alloys. There is indication from previous studies [9, 139, 144, 148, 155, 158-161] that the microstructure is dependent on the RE (Ce and La) elements and their concentrations (Al:RE ratio) as well as the cooling rate during solidification. However, the influence of RE and cooling rates on the microstructure development in these alloys remains unclear and hence further investigations are needed.

2.3 Effect of processing conditions on microstructure and properties of cast Mg alloys

Microstructure and phase selection during solidification is important, as the properties of an alloy strongly depend upon the intermetallic phases, especially in as-cast alloys. Microstructural features depend on the solidification parameters, such as cooling rate, and phase selection in Mg-Al-RE alloys is affected by alloying elements as well as alloying content. This section discusses the previous research work on the effects of cooling rate and rare earth alloying have on the microstructure development and properties in cast magnesium alloys.

2.3.1 Processing conditions on the microstructure of Mg-Al-RE alloys

The cooling rate is an important parameter in the solidification process because it affects the microstructure of the alloys by controlling the nucleation of phases and their subsequent growth. During the solidification of commercial magnesium alloys, such as AE44, primary α-Mg dendrites are commonly observed at the early stages of solidification [139, 156, 169]. The nucleation frequency of this primary α-Mg is often greater in HPDC (high pressure die-casting)
alloys due to high cooling rate and hence higher driving force for nucleation resulting in finer grain size in the subsequent grain growth [115].

Apart from the grain size, the secondary dendrite arm spacing (SDAS) is also highly affected by cooling rates during solidification [8, 170]. For example, a previous study [9] shows that dendrite arm spacing increases with decreasing cooling rates. Similarly, Turhal and Savaskan observed that the SDAS in Zn alloys decreases with increasing the cooling rate, as shown in Figure 2.21. Lu et al. [171] also reveal finer morphologies during rapid solidification; this includes grain size and SDAS. In addition, columnar dendrites were formed at slower cooling rates during steel mould casting, whereas equiaxed grains are developed in fast cooling during HPDC [12]. Two possible factors contribute to this situation: cooling rates and turbulence due to high-speed injection, which crushes the columnar dendrites even if they are formed during HPDC [12].

![Figure 2.21 The effect of cooling rate on the SDAS (d) of the Zn-40Al-1Cu, Zn-40Al-2Cu and Zn-40Al-3Cu alloys [172].](image)

The eutectic structure can also be influenced by the cooling rate. For example, Nave et al. [173] analysed the relationship between eutectic morphology and growth rate for various cooling rates. Finer eutectic grains along with a smaller interphase spacing shows that a fibrous morphology is observed at high growth rates, whereas lamellar eutectic structures appear at
slow growth rates [173]. Other studies [114, 174, 175] show that a high cooling rate (greater than 600 °C/min) leads to divorced eutectic morphology in the HPDC process, whereas a slower cooling rate develops partially divorced eutectic (Figure 2.22).

The type and distribution of intermetallic phases also largely depends on the solidification rate. For example, despite the phase diagram prediction of Mg$_{17}$Al$_{12}$ phase formation in Mg-Al based alloys, there is no Mg$_{17}$Al$_{12}$ found in AE42 during HPDC at a cooling rate of 200 °C/s. However, Mg$_{17}$Al$_{12}$ is found in the alloy after furnace cooling at 0.21 °C/s and in steel mould casting at 67 °C/s [12]. The same study also shows that the formation of a fine α-Mg + Al$_{11}$RE$_3$ eutectic structure is favoured at a high cooling rate. Whereas, the slower cooling rate promotes the formation of more Al$_2$RE in the AE42 alloy. According to the Al-Ce and Al-La binary phase diagrams, the thermal stability of Al$_2$RE is higher than that of Al$_{11}$RE$_3$; thus, Al$_2$RE formation in theory should be favoured at high cooling rates due to the increase in the thermodynamic driving force.

### 2.3.2 Properties of cast Mg-Al-RE alloys

#### 2.3.2.1 Factors influencing the castability of alloys

Magnesium alloys typically have high fluidity and less susceptibility to hydrogen porosity, hence better castability compared to aluminium alloys [176]. Since HPDC is the prominent manufacturing process for magnesium components [177], castability is one of the important design criteria in magnesium alloy development. It is known that the formation of eutectic morphology also affects the overall castability of Mg alloys. A previous study [151] indicates that solidification takes place at a wider temperature range provides a large volume of the
eutectic, which leads to better castability. The results from this study suggest that AE41 and AE91 have better castability because of their wider solidification range, however, AE21 has relatively poorer castability due to its narrow solidification range. Apart from this, the addition of rare earth elements in Mg-Al based alloys has the effect of refining grain size and reducing the amount of the undesired Mg$_{17}$Al$_{12}$ phase.

2.3.2.2 Creep resistance

Among all the commercial magnesium alloys, AZ91, AM60 and AM50, have been widely used in the automotive industry for non-critical parts such as seat frame and instrument panels. However, these commercially used alloys have relatively poor creep resistance at elevated temperatures more than 125–130 °C, which makes them unsuitable for operating at high temperatures such as those encountered in powertrain applications [133, 134, 149, 178, 179]. Factors which influence creep properties have been explored in several studies.

One factor believed to limit creep resistance is the appearance of the Mg$_{17}$Al$_{12}$ phase in Mg-Al based alloys upon solidification. The discontinuous phase of Mg$_{17}$Al$_{12}$ located at the grain boundaries is readily coarsened at elevated temperature, and hence the strengthening effect of this phase is reduced [136]. Therefore, effectively suppressing the formation of Mg$_{17}$Al$_{12}$ using other alloying elements such as rare earths can enhance the mechanical properties [179-181]. In Mg-Al-RE alloys, the concentration of rare earth directly impacts on the formation of Mg$_{17}$Al$_{12}$ phase. For example, the addition of 2-4 wt.% of cerium to a Mg-Al alloy results in the formation of Al$_{12}$Ce$_3$ and decreases the amount of Mg$_{17}$Al$_{12}$. Further analysis based on computational thermodynamics also shows that the formation of Mg$_{17}$Al$_{12}$ is completely suppressed when the cerium concentration is above 15 wt.% in a Mg-4Al based alloy (Table 2.9) [105].

Table 2.9 Scheil simulation of Mg-Al-Ce alloys showing suppression of Mg$_{17}$Al$_{12}$ with increasing cerium content [105].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>(Al,Mg)$_2$Ce</th>
<th>Al$_{12}$Ce$_3$</th>
<th>Mg$<em>{17}$Al$</em>{12}$</th>
<th>Mg$_{17}$Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>AM50</td>
<td>―</td>
<td>―</td>
<td>4.3</td>
<td>―</td>
</tr>
<tr>
<td>AE42</td>
<td>0.9</td>
<td>0.2</td>
<td>1.8</td>
<td>―</td>
</tr>
<tr>
<td>AE44</td>
<td>2.0</td>
<td>0.1</td>
<td>1.0</td>
<td>―</td>
</tr>
<tr>
<td>AE416</td>
<td>9.5</td>
<td>0</td>
<td>0</td>
<td>0.7</td>
</tr>
</tbody>
</table>

Previous investigations [149, 153, 171, 182-186] have characterised the effects of rare earth contents on microstructure development and mechanical behaviour of Mg-4wt.%Al alloy. The
results show that as the $\text{Al}_{11}\text{RE}_3$ phase increases, the $\text{Mg}_{17}\text{Al}_{12}$ reduces, which improves the creep resistance effectively. Another study [149] also investigated the effects of RE additions by adding cerium to Mg-4Al based alloys. It was found that 4 wt.% of cerium exhibits an optimal cost:performance ratio among all the cerium concentrations. This highlights why AE44 is currently used for commercial applications rather than other AE alloys. This is also supported by Asl et al. [187], as Figure 2.23 shows that AZ91 containing 3 wt.% rare earth element possesses the best creep properties compared to AZ91 without rare earth and AZ91 with 2 wt.% rare earth. This agrees with the study by Chaubey et al. [186], which shows that the $\text{Mg}_{17}\text{Al}_{12}$ intermetallic phase is completely diminished and replaced by both the $\text{Al}_{11}\text{Ce}_3$ and $\text{Al}_2\text{Ce}$ intermetallic phases in Mg-Al-Ce alloys with cerium content above 3 wt.%.

![Figure 2.23 Creep rates of alloys with different applied stresses at 200 °C [182].](image)

Additionally, it has been proposed that the saturated aluminium solute in the eutectic $\alpha$-Mg contributes to the poor creep resistance, and this may be due to microstructure instability [141, 188]. Previous studies also attribute the decrease in creep resistance at elevated temperatures to a decrease in volume fraction of eutectic $\text{Al}_{11}\text{RE}_3$ marked by a simultaneous increase in $\text{Al}_2\text{RE}$ and the formation of $\text{Mg}_{17}\text{Al}_{12}$ [144, 189]. One thing that needs to be considered is that even though the preferential reaction is for aluminium and rare earth elements to form $\text{Al}_{11}\text{RE}_3$ and $\text{Al}_2\text{RE}/\text{Al}_3\text{RE}$ phases in die-cast AE alloys, it is still possible for $\text{Mg}_{17}\text{Al}_{12}$ to precipitate at elevated temperatures. This is due to the supersaturation of aluminium in the $\alpha$-Mg matrix after die-casting [190].

Apart from suppressing the thermally unstable $\text{Mg}_{17}\text{Al}_{12}$ phase to achieve better creep performance, it is also found that the presence of $\text{Al}_{11}\text{RE}_3$ can improve the creep properties by enabling the pinning of grain boundaries and thereby hindering both the migration of grain
boundaries and sliding at high temperatures [149, 182, 184], as shown in Figure 2.24. In a separate study, Bell and Langdon [191] also claim that grain boundary sliding contributes to the creep deformation, which can be up to 80% of the total deformation for a Mg-0.78Al alloy. Bai et al. [156] also assert that grain boundary sliding is a possible controlling mechanism responsible for creep deformation at elevated temperatures. In addition, it has been shown that divorced eutectic formation is most likely to be beneficial for creep resistant alloys. This is due to the presence of the intermetallic phases in the grain boundaries is more resistant to deformation at elevated temperatures [114].

![Figure 2.24 SEM Images of (a) AZ91 (b) AZ91 with 2 wt.% rare earth in the 24 hours annealed condition [184].](image)

Despite the boundary sliding mechanism in creep improvement being widely discussed, an increasing number of studies have considered other factors, in particular the relationship of supersaturation and the strengthening effects for creep deformation [192, 193]. While the role of near grain boundary reinforcement on creep behaviour remains a subject of debate, Zhu et al. [190, 194] argue that rare earth solute supersaturated in the α-Mg matrix, as well as precipitation, are the main factors contributing to creep resistance instead of grain boundary reinforcement through intermetallic phases for die-cast Mg-RE alloys.

In RE-rich alloys, alloys with neodymium and yttrium possess better creep resistance for powertrain components than those with La and Ce [161]. Another comparison study also observed that Mg-Nd alloys are the most creep resistant and Mg-La alloys are the least creep
resistant compared with Mg-Nd and Mg-Ce binary alloys [194]. This finding may not be applicable to ternary Mg-Al-RE alloys, as the Al$_{11}$La$_3$ phase developed in the ternary Mg-Al-La system is reported to have better thermal stability at the grain boundaries compared to Al$_{11}$RE$_3$ in Mg-Al-RE system (where RE refers to cerium-rich mischmetal) [133, 134], as highlighted in Table 2.10. It is also reported that the selection of the rare earth elements has a great influence on the creep resistance of AE alloys. The difference in creep resistance is attributed to the different thermal stability of Al$_{11}$RE$_3$, of which Al$_{11}$La$_3$ is the most stable, followed by Al$_{11}$Ce$_3$, and Al$_{11}$Nd$_3$ being the least stable [141, 163].

<table>
<thead>
<tr>
<th>Temperature (˚C)</th>
<th>AE44 UTS (MPa)</th>
<th>AE44 YS (MPa)</th>
<th>AE44 ε (%)</th>
<th>ALa44 UTS (MPa)</th>
<th>ALa44 YS (MPa)</th>
<th>ALa44 ε (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>247</td>
<td>140</td>
<td>11</td>
<td>264</td>
<td>146</td>
<td>13</td>
</tr>
<tr>
<td>120</td>
<td>172</td>
<td>126</td>
<td>22</td>
<td>182</td>
<td>128</td>
<td>23</td>
</tr>
<tr>
<td>150</td>
<td>145</td>
<td>110</td>
<td>25</td>
<td>148</td>
<td>112</td>
<td>27</td>
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<tr>
<td>175</td>
<td>123</td>
<td>107</td>
<td>26</td>
<td>135</td>
<td>108</td>
<td>25</td>
</tr>
<tr>
<td>200</td>
<td>115</td>
<td>105</td>
<td>23</td>
<td>118</td>
<td>102</td>
<td>20</td>
</tr>
</tbody>
</table>

In the literature, it is interesting that a few studies [137, 144, 164] find that the formation of Al$_2$RE at slow cooling rate shows no improvement in creep performance, whereas the formation of Al$_{11}$RE$_3$ at high cooling rates does improve creep performance. Theoretically, Al$_2$RE with grain refining capability should show improvement in mechanical properties, but not in this case. It is likely that other factors, such as the cooling rate, overtakes the potent nucleant effect in controlling the creep properties. On the other hand, it is sometimes better to have a large grain size for improvement in creep but casting alloys can show opposite behaviour. Hence, this is difficult to be too predictive and the mechanism behind this phenomenon remains a subject of debate.

2.3.2.3 Room temperature strength and ductility

There have been several notable literature reviews on how the microstructure affects the mechanical properties of Mg alloys. Factors like the grain size, SDAS, morphology, secondary phase distributions and type of intermetallic phase as well as the alloying selection, have a direct influence on the alloy properties, such as strength and ductility.
While there are many studies showing that higher rare earth concentration leads to increased intermetallic phases and hence improves the properties of the alloys [141, 144, 189, 195], interestingly other studies show negative effects of having too high concentrations of rare earths. For example, one study [196] shows that low rare earth concentration can refine both the dendrite and grain size. However, higher rare earth concentrations result in grain coarsening which is attributed to the decrease in aluminium contribution to grain refinement. Similarly, Khomamizadeh et al. [185] also show that the additions of rare earth elements with more than 3 wt.% in Mg-Al based alloys reduce the strength and ductility. This is due to the brittle characteristic of the Al\textsubscript{11}RE\textsubscript{3} phase with sharp needle-like morphology. Additionally, Lu et al. [171] demonstrated that the addition of too much rare earth causes the coarsening of Al\textsubscript{11}RE\textsubscript{3}, but it has minor benefit for the mechanical properties of the alloy.

On the other hand, one of the key microstructure features that can greatly influence the properties is SDAS. For example, a previous study [172] shows hardness increases when the SDAS is decreased at a high cooling rate, as shown in Figure 2.25. In the later stages of the solidification process, the eutectic phase is also an important microstructural feature that influences the alloy properties [115]. This is because the eutectic has strong interfacial bonding, which is capable of transferring a load from one phase to another and hence the strengthening effect is increased [197]. In Mg-Al based alloys, it is known that intermetallic phases in ductile materials can improve the strength [11, 198-200]. In addition, the morphology and distribution of intermetallics may also effect alloy strengthening mechanisms [11, 121]. Previous studies [11, 116] also claim that the addition of alloying leads to the increase of solute content in solid solution, and hence improve the strength of the alloys. It is worth mentioning that the low solid solubilities of RE in Mg-La and Mg-Ce systems causes an insignificant contribution to solid solution strengthening of these alloys [11].
2.3.3 Grain refinement for strengthening mechanical properties

It is also well established that the mechanical properties and structural homogeneity are often improved in most metal alloys with the presence of fine grain size [201]. Therefore, grain refinement in casting is especially important for the performance of the cast products. Grain refinement can be challenging, as only a small fraction of the grain refiner particles successfully act as heterogeneous nucleation sites, whereas the majority of the grain refiner particles are segregated between the dendrite arms or along the grain boundaries [202]. A grain refiner can act as a potent nucleant when the interfacial energy between the nucleant particles and the newly forming solid is low. A potent nucleant corresponds to the occurrence of nucleation at low critical supercooling ($\Delta T_n$). This means the lower the $\Delta T_n$, the higher potency of the nucleant [203]. It has also been reported that constitutional undercooling, which is influenced by both the alloy composition and cooling, controls both the grain size and SDAS [170].

The key factors controlling grain refinement are the nucleant particles including their potency, size distribution and particle number density, and the rate of development of growth restriction, $Q$, in which the undercooling established is required to trigger nucleation events and facilitate their survival during the growth process [204]. Previous studies [203, 205-207] suggest that a good potent nucleant should have good crystallographic matching with the primary matrix.

Figure 2.25 The effect of SDAS ($d$) on the hardness of Zn-40Al-1Cu, Zn-40Al-2Cu and Zn-40Al-3Cu alloys [172].
phase. This relationship minimises the interfacial energy between the nuclei and the matrix. Other researchers propose that the size of inoculant particles should be larger than the critical threshold for nucleation [203, 208].

Zirconium is a popular grain refiner in Mg alloys, which is also the most potent nucleant introduced for commercial aluminium-free magnesium-based alloys [209]. However, it is only suitable for aluminium-free alloys due to the high reactivity between aluminium and zirconium leading to the formation of intermetallic phases with aluminium [203]. More to the point is that given the great importance of grain size, there has been a lot of research focusing on discovering potential grain refiners and optimising the existing grain refiners.

In microstructure and morphology, there remain multiple challenges that require research effort. One of these challenges is the nucleation crystallography of the very first step upon the microstructure forming process. Several geometric crystallographic models have been developed to understand the various types of grain refiner effects on grain refinement: namely the linear disregistry model [210], planar disregistry model [206] and edge-to-edge matching model (E2EM) [211, 212]. Experimental studies remain highly challenging due to the difficulty in obtaining active nucleants in within the grains. The difficulty in finding the active nucleants due to their scarcity in grains often complicates nucleation studies. However, synchrotron studies using high energy X-rays enables the observation and study of individual grains in bulk materials [213-215]. For example, Iqbal et al. [213] observed the grain nucleation and grain growth of aluminium alloys using this technology. In addition, they demonstrated the significance of the metastable phase in the enhancement of grain nucleation in liquid aluminium alloys. From this study, the theoretical model of solidification predictions is verified through in-situ experiments [213].

Apart from that, a study proved a feasible way to investigate nucleation crystallography between the active nucleant and metal nuclei in a real casting is to use Focus-Ion-Beam (FIB) aiding the TEM [216]. Al₂Y particles have been confirmed to be the effective grain refiner for Mg-Al-Y alloys using the FIB aided TEM method as well as E2EM crystallography matching [202, 216, 217]. Furthermore, the grain refining efficiency of Al₂Y has exceeded the performance of the current popular grain refiner, zirconium. This is because the grains refined by Al₂Y have greater thermal stability compared to those refined by zirconium, under the conditions of 550 °C for 48 hours [202]. In other words, grain coarsening during heat treatment
occurs more rapidly when grains are refined by zirconium compared to grains that are refined by Al$_2$Y.

Besides the Al$_2$Y being a potent nucleant, Jiang et al. [218] showed that Al$_2$Ce is also a potent nucleant for the Mg-Al-Ce system using crystallographic calculations. Similarly, microscopic observations and crystallographic calculations also indicate that Al$_4$Ce is a potential nucleant for $\alpha$-Mg grains by promoting heterogeneous nucleation of $\alpha$-Mg on Al$_4$Ce particles [219]. This agrees with another study that observed a grain refinement effect with the addition of cerium into a Mg-20Zn-8Al alloy [220]. Qiu et al. performed a series of interfacial energy calculations and the result indicated both Al$_2$Y and Al$_2$Ce are effective nucleants according to these calculations, although Al$_2$La is not predicted to be effective (Figure 2.26) [216]. Although the preliminary understanding of the principles of grain refinement in magnesium alloys has improved significantly and a range of potential grain refiners have been identified, a reliable master alloy for grain refinement of Mg-Al alloys remains to be developed.

![Figure 2.26 Wettability of potential inoculants in Mg-Al-RE alloys [216].](image)

### 2.4 Summary

The review of the literature focused on the solidification and microstructure development in Mg-Al-RE alloys. The three main gaps from the literature are:

1. The current Mg-Al-RE phase diagrams are largely based on extrapolations from the relevant binary systems. There are some discrepancies in the literature which suggest that this is not accurate. For example, the intermetallic phase stability in the Mg-Al-Ce and Mg-Al-La systems remains unclear. There are various liquidus temperatures also reported in these systems. To date, there are limited studies on the ternary Mg-Al-RE
systems, in particular the Mg-Al-La system. It is therefore of great importance to
determine and clarify the solidification sequence and hence contribute research data to
improve the thermodynamic database for Mg-Al-RE systems.

2. It was noted that there are debates and uncertainties on the intermetallic phases
developed in Mg-Al-RE alloys. Often all rare earth alloying elements are assumed to
behave in a similar way whilst the microstructure and properties appear to be different.
In addition, the literature shows that the microstructure is dependent on the cooling rate
during solidification, but the relationship of the influences on the microstructure is
unclear. Hence, the research in this thesis will focus on understanding the effects of
individual rare earth elements and cooling rates on the phase selection and
microstructure development in Mg-Al-RE alloys.

3. In casting, there are several factors which influence properties, including grain size,
SDAS, intermetallic type and amount of intermetallic phase. However, the
microstructure-properties relationship is unclear. Therefore, a systematic study of the
effects of alloying element, concentration and cooling rate is needed to better
understand the interdependence relationship between processing-microstructure-
properties in Mg-Al-RE alloys.

From the research gaps identified, three areas of focus have been identified and these have been
the motivations of the research undertaken in this thesis. These gaps are investigated in the
subsequent Chapters 4 to 9. The results from these studies provide better understanding of how
to effectively control and select the microstructure and intermetallic phases of Mg-Al-RE
alloys. A summary of the research gaps and focus in this thesis is shown in Figure 2.27.
### Literature review gaps

1. Lack of comprehensive thermodynamic database for Mg-Al-RE alloys. In particular, the current Mg-Al-La and Mg-Al-Ce thermodynamic database, e.g. solidification sequence and phase diagram is contradictory and inconsistent with experimental results.

2. Ce and La are assumed to behave similarly in microstructure development during solidification process. The microstructure characterisation in these alloys are ambiguous. In addition, the literature reported mainly on the binary Al-RE and Mg-RE intermetallic phases in the Mg-Al-Ce and Mg-Al-La systems, but relatively less study on ternary phase, such as whether Mg dissolve in the binary Al-RE intermetallic phase. It is also often assumed Al-Ce phase as analogous to that of Al-La phase.

3. There is uncertainty of the effects of cooling rate on microstructure, e.g. the exact phase development in a certain compositions alloy at low and high cooling rates remains a debate in the literature.

### Research Questions

1. What is the solidification sequence and the validity of the current phase diagram of Mg-Al-Ce and Mg-Al-La systems?

2. Is the morphology different in Mg-Al-La and Mg-Al-Ce alloys? If so, why is the morphology in Mg-Al-La alloys different to Mg-Al-Ce alloys? How do rare earth selections (Ce and La) affect the microstructure development in Mg-Al-RE alloys?

3. How does solidification conditions (i.e. cooling rate) affect the microstructure development and properties in Mg-Al-RE alloys?

### Hypothesis

1. The inconsistencies in Mg-Al-Ce and Mg-Al-La systems lead to inaccurate thermodynamic predictions, which will require more experimental work to improve the accuracy of the database.

2. The difference in the morphology in Mg-Al-Ce and Mg-Al-La alloys can be due to the formation of different phases. However, if they are formed as the same phase, the difference in morphology may be attributed to:
   - Diffusion rates;
   - Physical or chemical restrictions on microstructure growth;
   - Crystallography effects, such as same crystal structure but different lattice parameters;
   - Proportion of phases, such as the amount of α-Mg and intermetallic phase in eutectic.

3. The development of microstructure can be controlled by varying cooling rates. Metastable phase can be formed at high cooling rate conditions. Ultimately, material properties can also be refined to suit for specific applications by controlling phase selections through solidification process.

### Importance

1. A consistent thermodynamic database provide greater accuracy of predictions, which can be better used in alloy design and optimisation for magnesium alloys.

2. The role of RE can form a basis of phase selection in the alloy. The microstructure and experimental work can also contribute to the thermodynamic and crystallographic database.

3. Cooling rate can be the starting point in understanding the solidification behaviour, especially most commercial magnesium alloys are die-casting. The processing–microstructure–properties relationship can be used to predict and compare the microstructure features and properties for the studied range of Mg-Al-RE alloys.
2.5 References


77. A. Saccone, et al., *Phase equilibria in the rare earth metals (R)-rich regions of the R-Al systems (R = La, Ce, Pr, Nd)*. Zeitschrift fuer Metallkunde, 1996. 87(2): p. 82-87.


Chapter 2 Literature Review


Chapter 3

Methodology
3 Chapter 3: Experimental materials and methodology

This chapter summarises the experimental techniques used to produce and characterise the Mg-Al-RE samples studied in later chapters. Further details specific to individual experiments can be found in the corresponding chapters.

3.1 Alloy preparation by gravity casting

The samples analysed in the present work include the experimental alloys with nominal compositions: ACe44, ACe47, ACe410, ACe413, ALa44, ALa47, ALa410, and ALa413. The selection of these alloys was based on the commercial alloy, AE44, and alloying contents that are closer to the phase boundary in the phase diagrams. These alloys were cast in two batches. The alloys were prepared from pure elemental magnesium (99.95 %), aluminium (99.90 %), cerium (99.50 %) and lanthanum (99.90 %). The molten magnesium alloys were cast into a wedge mould consisting of two parts, a sand mould and a permanent mould as shown in Figure 3.1. The reason for using a wedge-shaped mould is that it creates a wide range of cooling rates in a single casting, and the combination of sand wedge and permanent mould wedge further extends the cooling range.

![Figure 3.1 Wedge mould equipped with three thermocouples attached directly to the permanent steel mould to monitor the mould temperature. Seven additional thermocouples were set up inside the mould to have direct contact with the alloy.](image)

The alloys were melted under 98 % nitrogen mixed with 2 % R134a refrigerant gas. The melting and pouring temperatures of the molten metal were 720 °C for ALa44, ACe44, ALa47 and ACe47 alloys and 800 °C for ALa410, ACe410, ALa413 and ACe413 alloys. This is because the liquidus temperature increases with increasing cerium (Ce) and lanthanum (La) contents in the alloys. The alloys were stirred well after each addition, to ensure complete mixing. The mould was preheated to 120 °C and the molten alloy was poured into the mould.
when the mould temperature reached approximately 95 °C. The cast alloys were solidified to room temperature before removing from the mould.

K-type thermocouples were placed at seven locations along the centreline of the wedge mould and were retained within the final cast samples, as shown in Figure 3.2. X-ray radiographs were then used to verify the actual thermocouple locations in the solidified samples. The temperatures of the seven thermocouples were recorded every 100 ms using a digital data acquisition system. The chemical compositions of the alloys were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), the results of which are given in Table 3.1.

Figure 3.2 Sample was cast into a wedge-shaped mould consisting of two parts: sand mould (left) and permanent mould (right).

Table 3.1 Composition of the experimental wedge cast alloys in two separate batches, all compositions are in weight percent (wt.%).

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Chemical analysis</th>
<th>Nominal compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
<td>Ce</td>
</tr>
<tr>
<td>ACe44</td>
<td>-</td>
<td>3.73</td>
</tr>
<tr>
<td>ACe47</td>
<td>-</td>
<td>6.60</td>
</tr>
<tr>
<td>ACe410</td>
<td>-</td>
<td>10.1</td>
</tr>
<tr>
<td>ACe413</td>
<td>-</td>
<td>12.4</td>
</tr>
<tr>
<td>ALa44</td>
<td>4.10</td>
<td>-</td>
</tr>
<tr>
<td>ALa47</td>
<td>7.08</td>
<td>-</td>
</tr>
<tr>
<td>ALa410</td>
<td>10.3</td>
<td>-</td>
</tr>
<tr>
<td>ALa413</td>
<td>13.8</td>
<td>-</td>
</tr>
</tbody>
</table>

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3.2 Sample preparation for microstructural study

3.2.1 Sample preparation for EDX, SEM and EBSD imaging

Sample preparation for microstructural studies involved multiple procedures including sample cutting, grinding and polishing. The as-cast wedge samples were first sectioned along the centreline, close to the plane on which the thermocouples were located. Seven smaller samples were then cut from each wedge, in locations corresponding to the different thermocouples, as shown in Figure 3.3.

The samples were then cold mounted using epoxy resin and hardener with a mixing ratio of 15 parts of resin to 2 parts of hardener. The mixture of resin and hardener was stirred for at least 10 minutes to ensure complete mixing, which is important for the epoxy resin to set. After placing the epoxy resin and sample in the mould, the samples were left overnight to set at room temperature. Lastly, the cold mounted samples were placed in an oven at 60°C for an hour to complete the process. The reason for using cold mounting only and not hot mounting in this study is to minimise the possibility of microstructural change due to the high temperatures involved in the hot mounting process. The mounted samples were then polished for microstructural analysis, allowing the effects of cooling rate and alloy composition to be studied.

(b) Second batch of castings

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Chemical analysis</th>
<th>Nominal compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
<td>Ce</td>
</tr>
<tr>
<td>ALa44</td>
<td>3.81</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>ACe44</td>
<td>3.87</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>ACe413</td>
<td>&lt;0.005</td>
<td>13.1</td>
</tr>
<tr>
<td>ALa413</td>
<td>13.4</td>
<td>0.005</td>
</tr>
</tbody>
</table>

Alloys

- ALa44
- ACe44
- ACe413
- ALa413

Chemical analysis

La, Ce, Al, Mn, Mg

Nominal compositions

La, Ce, Al, Mg
Chapter 3 Methodology

For microstructure characterisation, the cold mounted samples needed polishing to a high surface finish. The challenge in preparing magnesium alloys is their sensitivity to corrosion in contact with water, which limits the use of water-based lubricants during grinding and polishing. In the present sample preparation procedure, no water was involved throughout the grinding and polishing process. All lubricant and polishing suspensions used on the alloys were alcohol-based solutions.

Figure 3.3 Locations of the seven samples cut from the wedge castings for microstructural studies.
During grinding, the cold mounted samples were first ground with silicon carbide (SiC) papers with a grit number of 400 and then 600, using a Struers RotoForce-21 grinding and polishing machine with an automated mode set at 300 rpm. Due to the softness of magnesium, a layer of wax was also applied on to the SiC paper to avoid excessive grinding. Each of these grinding steps was carried out for 1.5 minutes. An alcohol-based DP-Brown lubricant was used as the coolant during grinding.

After grinding, the samples were polished using the same polishing machine on automatic mode. The first polishing was carried with a 9 μm diamond suspension using a Struers MD-Largo polishing cloth for 6 minutes, followed by a 3 μm diamond suspension using a MD-DAC polishing cloth for 7.5 minutes, and a 1 μm diamond suspension using a MD-Nap polishing cloth for 3 minutes, all on 150 rpm. The DP-Brown lubricant was used for 9 μm polishing, and DP-Yellow lubricant was used for the 3 μm and 1 μm polishing. The turntable of the machine was rotated in the same direction as the sample holder for all of these steps.

The final polishing was on a 0.04 μm colloidal silica suspension using a MD-Chem polishing cloth for 1.5 minutes at 150 rpm. The rotations of the turntable and sample holder were set to counter rotation. Ethanol was used as the lubricant in this step. The samples were cleaned ultrasonically for 180 seconds after each step to remove excess silica residue, and the final polished samples were cleaned with ethanol and dried with compressed air before storing in a vacuum jar. Table 3.2 shows the details of each grinding and polishing steps for the Mg-Al-RE alloys used in this study.

Table 3.2 Sample preparation procedure using a Struers RotoForce-21 polishing machine, “>>” is the co-rotation and “><” is the counter-rotation of the turntable. *OPS solution is a mixture of 50 % OPS (oxide polishing suspensions) and 50 % Ethanol.

<table>
<thead>
<tr>
<th>Step (L-R)</th>
<th>Grind</th>
<th>Polish - 9μm</th>
<th>Polish - 3μm</th>
<th>Polish - 1μm</th>
<th>Polish - OPS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface/Cloth</td>
<td>SiC #400 &amp; 600 + Wax</td>
<td>MD-Largo</td>
<td>MD-DAC</td>
<td>MD-Nap</td>
<td>MD-Chem</td>
</tr>
<tr>
<td>Abrasive Type</td>
<td>-</td>
<td>DP-Susp. A. 9 μm</td>
<td>DP-Sus. A. 3 μm</td>
<td>DP-Yellow</td>
<td>OPS*, 0.04 μm</td>
</tr>
<tr>
<td>Lubricant Type</td>
<td>DP-Brown</td>
<td>DP-Brown</td>
<td>DP-Yellow</td>
<td>DP-Yellow</td>
<td>Ethanol</td>
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<tr>
<td>Lubricant Spray (s)</td>
<td>Every 5 s</td>
<td>Every 15 s</td>
<td>Every 15 s</td>
<td>Every 15 s</td>
<td>Every 2 s</td>
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<tr>
<td>Speed (rpm)</td>
<td>300</td>
<td>150</td>
<td>150</td>
<td>150</td>
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</tr>
<tr>
<td>Force (N)</td>
<td>20</td>
<td>25</td>
<td>20</td>
<td>15</td>
<td>10</td>
</tr>
<tr>
<td>Holder Direction</td>
<td>&gt;&gt;</td>
<td>&gt;&gt;</td>
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<td>&gt;&gt;</td>
<td>&gt;&gt;</td>
</tr>
<tr>
<td>Time (min)</td>
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<td>6:00</td>
<td>7:30</td>
<td>3:00</td>
<td>1:30</td>
</tr>
</tbody>
</table>
Chapter 3 Methodology

For EBSD analysis a mirror finish is required to obtain a good signal and special care needs to be taken to avoid oxidation or corrosion of the surface after polishing. The preparation procedure outlined in Table 3.2 was successful in producing the surface finish required for EBSD. However, the samples needed to be stored in a vacuum bell jar between polishing and analysis, to preserve the surface.

3.2.2 Sample preparation for X-Ray Powder Diffraction (XRD)

The epoxy resin mounted samples (Figure 3.3) were also used for XRD analysis. In other cases, some of the wedge cast samples were cut in half in both sections (permanent-cast and sand-cast samples), as shown in Figure 3.4, in order to expose the maximum surface area for analysis and hence improve the particle statistics in the XRD measurement. The cut surface was then polished to 1 micron for analysis.

During the investigation into the crystal structure of the (Al,Mg)₃La phase (Chapter 5), powdered samples were also prepared from a number of alloys. This enabled high-resolution synchrotron XRD data to be collected from a number of Mg-Al-La alloys, using the Powder Diffraction beamline [1] at the Australian Synchrotron. Magnesium alloy powders were obtained by a simple manual filling method. The powder samples were then sieved to between 45 µm and 125 µm particle size so that they could be loaded into a 0.3 mm capillary tube.

To relieve the stresses induced by the filing process, the sample powders were sealed into glass ampules under argon and heat treated at 350 °C for 2 hours before loading into the capillary tube. This ensured that the α-Mg peaks were relatively narrow, to minimise peak overlap with the intermetallic phases of interest.

Figure 3.4 Wedge cast sample cut in half for XRD.
3.3 Microstructure analysis

3.3.1 Microstructure characterisation

Microstructure characterisation was performed using a SEM equipped with EDX and EBSD detectors. Phase identification was carried out using XRD and TEM. The microstructural investigations include:

1. Characterisation of intermetallic phases and their morphologies (SEM, EDX and FIB-SEM)
2. Identification of intermetallic phases (XRD and TEM)
3. Quantification of microstructure features (SEM and imageJ)
4. Investigation of nucleant potency of Al-RE intermetallic particles (EBSD)

3.3.1.1 scanning electron microscope (SEM)

The microstructure features of the alloys were characterised using qualitative and quantitative methods. The phase morphology was observed qualitatively using an FEI Quanta 200 scanning electron microscope (SEM), equipped with an Oxford Instruments X-MaxN 20 energy dispersive X-ray (EDX) spectrometer at 25 kV. For SEM imaging, an optimal working distance of 10 mm from the sample inside the vacuum chamber was used. A spot size of 5 nm was also used for most of the microstructural investigation in this study. For the majority of the SEM imaging, secondary electron (SE) mode is used. In some circumstances, backscattered electron (BSE) imaging was also used to use the atomic contrast to assist in observing the microstructure.

3.3.1.2 SEM microstructure features analysis

The microstructure features observed in the SEM micrographs, such as grain size and secondary dendrite arm spacing (SDAS) were qualitatively analysed using the ImageJ [2] software package. The samples were etched using an acetic-picric acid solution in water so that the grain sizes can be seen under an optical microscope. The ASTM E112-13 standard for the general linear intercept method was applied for SDAS and grain size measurements. The SDAS was measured by the number of arms intercepting a straight line of a known length from the SEM micrographs. Approximately 70 secondary dendrite arms close to the thermocouple position in the wedge castings were counted and averaged for each alloy. As for the grain size, a linear pattern was drawn over the grains and wherever a grain boundary would intercept any of the lines it was counted. Approximately 50-100 grain boundaries were measured for grain size measurement.
3.3.1.3 **Focus ion beam scanning electron microscope (FIB-SEM)**

Three-dimensional microstructure imaging is of great help for visualising the morphology of intermetallic phases observed microstructure. A FIB-SEM Scios DualBeam instrument was employed to obtain images of the three-dimensional topology of rare earth-containing intermetallic phases, as shown in Figure 3.5, by using the auto slice and view method. A typical slice and view technique is shown in Figure 3.6. During the auto slice and view, a high energy Gallium ion beam was used to slice a layer, then an electron beam was used for imaging. The Gallium ion beam current used in this experiment was around 13 nA. For three-dimension reconstruction, approximately 300 slices were taken, and images were collected after each slice. The images were then compiled using Fiji [3], which is an open source image analysis software.

![Figure 3.5 Three-dimensional topology of intermetallic phases.](image)

![Figure 3.6 A typical slice and view technique [4].](image)

3.3.1.4 **Electron backscattered diffraction (EBSD)**

An FEI Nova NanoSEM scanning electron microscope equipped with energy dispersive X-ray spectroscopy (EDX) and electron backscatter diffraction (EBSD) detectors was used to determine chemical and crystallographic information of the phases present in the alloys to determine whether or not intermetallic phases located in the centre of the grains could be potent nucleants for $\alpha$-Mg (Figure 3.7). An EDX detector was used to determine the constituent
elements that are present in the alloys, whereas the EBSD detector was used to identify phases by obtaining information on the crystallographic indices and Kikuchi patterns. During EBSD mapping, the sample in the vacuum chamber was placed with a working distance of approximately 10 mm and a tilt angle of 70°. To obtain good data, the input count was maintained at around 1000 counts per second and the dead time was kept at 30% during the measurement. EDX mapping and point scan were employed in this study. EBSD and EDX data were obtained through the Aztec software package [5]. The EBSD data including the associated Kikuchi patterns, were analysed using HKL Channel 5 (HKL Technology, Denmark).

![Figure 3.7 EBSD Kikuchi pattern of Al₅La₂ for potent nucleant investigation.](image)

### 3.3.2 Phase identification

The primary phase identification technique used in this study for all the as-cast samples is the XRD approach. XRD measurements were performed on bulk samples and powder samples depending on the XRD instrument and sample selection. Conventional laboratory XRD data were collected using Bruker D8 and Rigaku Smartlab diffractometers, whereas, synchrotron powder diffraction was used to collect high resolution XRD patterns.

#### 3.3.2.1 X-ray powder diffraction (XRD)

To identify the phases in the as-cast samples, XRD measurements were performed on both bulk and powder samples using a Bruker D8 diffractometer. This instrument was equipped with a Cu X-ray tube operated at 40 kV and 40 mA, and the data were collected between the range of 5-130° 2θ with a scan rate of 2°/min and a step size of 0.02°. Details specific to the experimental setup are also described in Chapters 4, 5, 6 and 7.

Bulk identification of the phases was also undertaken using a Rigaku Smartlab diffractometer, which was fitted with a rotating Cu anode operated at 45 KV and 200 mA. This instrument was
also equipped with a large area detector, which was used to intercept as much of the Debye-Scherrer rings as possible in order to improve the particle statistics, particularly from the α-Mg phase. During the XRD measurement, the sample was continuously oscillated ± 360° about the φ axis to further improve the particle statistics. Data were collected over the range 15-120° 2θ with an equivalent scan rate of 2°/min and a step size of 0.02°, as shown in Figure 3.8. The details of the XRD experiment can be found in Chapter 8.

![Figure 3.8 XRD measurement with a sample setup in the Rigaku Smartlab.](image)

The high-resolution powder diffraction beamline at the Australian Synchrotron [1] was also used to aid with structure refinement of the (Al,Mg)₃La phase. A monochromatic X-ray beam of 18 keV was used and measured over the angular range between 2-82.5° 2θ. The details of this experiment are outlined in Chapter 5.

### 3.3.2.2 XRD data analysis

The acquired XRD patterns were analysed using a combination of the Pawley [6] and Rietveld [7] methods through the Topas software package (version 5, Bruker). The structure models for the present phases in the alloys were taken from the Pearson handbook [8] and the ICDD PDF-4+ database [9].

### 3.3.2.3 Transmission electron microscopy (TEM)

The intermetallic phases in the alloys were also identified using a JEOL 2100F transmission electron microscope (TEM), equipped with an Oxford X-MaxN 80T EDX spectrometer. Plates of 0.5 mm thickness were cut from the bulk sample and discs of 3 mm diameter were punched from the plates. The discs were then ground to 50 μm. The TEM foils were then polished by low-angle ion milling using a Gatan Precision Ion Polishing System (PIPS) at 4 kV with an
Chapter 3 Methodology

incident angle of ±4° until perforation of the foil; then followed by beam energy of 2.5 kV and beam angle of ±2° for 30 minutes. The sample stage was not cooled during ion milling because there was no phase transformation expected to occur at temperatures below 150 °C for the intermetallic phases in the studied alloys.

The chemical composition of intermetallic phases was determined from the thin area of the foil using a focused electron beam in order to minimise the thickness effect and the interference of the surrounding matrix. The settings for the EDX analysis were based on a condenser aperture of 100 μm, spot size of 6-8 and acquisition time of 60 s. There were at least five particles analysed for each intermetallic phase.

Conventional selected area diffraction (SAED) or micro-beam electron diffraction (MBED) techniques were used to obtain the diffraction patterns, depending on the particle size of intermetallic phases. The settings for the MBED were based on a condenser aperture of 30 μm and a spot size of 6-8. Three patterns were normally recorded for a known intermetallic phase. However, more patterns were recorded for a new intermetallic phase for structure determination. The TEM work was performed by one of the author’s co-supervisors, Dr. Suming Zhu.

3.4 Solidification behaviour

In order to understand the solidification behaviour of magnesium and other cast alloys, it is useful to compare experimental temperature measurements with thermodynamic simulation results. Cooling curve thermal analysis (CCA) measurements were performed to obtain insights into the solidification features of the alloys, including the solidification temperature and the rate of solidification. Solidification was also observed in real-time via an in-situ synchrotron radiography experiment at the SPring-8 synchrotron facility in Japan. The experimental data were used to compare with Pandat® simulations.

3.4.1 Thermal analysis

In addition to the microstructural analysis described earlier, the effects of cooling rate and rare earth alloying concentrations were also studied by thermal analysis techniques. Computer-aided cooling curve thermal analysis (CA-CCA) of the studied alloys was carried out by solidifying the molten alloys in the wedge mould with seven K-type thermocouples positioned at different heights within the mould. The alloys were melted in a furnace and poured into a wedge mould, letting the melt solidify to room temperature, as described in Section 3.1. During
solidification, the temperature variations in the alloy were measured at the seven thermocouple locations along the wedge casting. These thermocouples were attached to a high-speed Picolog data acquisition system. The temperature data was translated into a cooling curve through the Picolog analysis software. The cooling curves (T-t) and their first derivative curves (dT/dt) were plotted using the software. The reproducibility of the individual measurements from the thermocouples was confirmed by repeating at least 2 times. The details of selecting the starting point of the reaction are explained elsewhere [10], and the details of the thermal analysis experiment are well described in Chapter 9.

3.4.2 In-situ synchrotron radiography
To observe the real-time solidification process, in-situ synchrotron radiography experiments were performed on the ALa314 alloy at the SPring-8 synchrotron in Hyogo, Japan (beamline BL20B2). The polished sample was held between two MgO plates, which then sit in between two alumina plates. This setup was then retained by a sample holder, consisting of BN plates. The sample holder was placed in a furnace, where there is a window for the synchrotron X-ray beam to pass through. The setup of the experiment and the sample configuration is shown in Figure 3.9. The details sample preparation and experimental setup are outlined in Chapter 6 [11].

![Figure 3.9](image)

Figure 3.9 (a) Experimental setup and (b) sample configuration for in-situ synchrotron radiography at BL20B2 beamline at SPring-8 [12].

3.5 Thermodynamic calculations
Thermodynamic calculations and phase diagrams were simulated using the PanMagnesium 2018 [13] database in Pandat®. The liquidus projection for Mg-Al-La system and Mg-Al-Ce system are shown in Figure 3.10. The solidification predictions were calculated using both the Scheil-Gulliver (non-equilibrium) and the Lever (equilibrium) conditions. The calculated
solidification characteristics were used to compare with the experimental results in the present research.

Figure 3.10 Liquidus projection of (a) Mg-Al-La system and (b) Mg-Al-Ce system generated by Pandat® PanMagnesium 2018 [13].
3.6 References


Chapter 4

Experimental study of the solidification microstructure in the Mg-rich corner of Mg–Al–Ce system

Charlotte Wong\textsuperscript{a}, Mark J. Styles\textsuperscript{b}, Suming Zhu\textsuperscript{a}, Trevor Abbott\textsuperscript{a,d}, Kazuhiro Nogita\textsuperscript{c}, Stuart D. McDonald\textsuperscript{c}, David H. StJohn\textsuperscript{c}, Mark A. Gibson\textsuperscript{a,b}, Mark A. Easton\textsuperscript{a}

\textsuperscript{a} School of Engineering, RMIT University, Carlton, Victoria 3053, Australia

\textsuperscript{b} CSIRO Manufacturing, Clayton, Victoria 3168, Australia

\textsuperscript{c} School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia

\textsuperscript{d} Magontec Limited, Sydney, New South Wales 2000, Australia

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Experimental Study of the Solidification Microstructure in the Mg-Rich Corner of Mg–Al–Ce System

Charlotte Wong, Mark J. Styles, Suming Zhu, Trevor Abbott, Kazuhiro Nogita, Stuart D. McDonald, David H. StJohn, Mark A. Gibson, and Mark A. Easton

Abstract

The current lack of comprehensive understanding of the microstructure evolution in Mg–Al–Ce alloys hinders the accuracy of thermodynamic predictions. Our investigations have identified shortcomings within the published literature for the Mg-rich end of the Mg–Al–Ce phase diagram. In this study, the microstructure evolution in Mg–Al–Ce alloys has been studied by X-ray diffraction, scanning and transmission electron microscopy. The experimental results are compared with the Scheil-Gulliver prediction calculated using the CALPHAD method. The observed microstructure contains both the binary Al–Ce and Mg–Ce intermetallic phases in these alloys. The solidification sequence, invariant point and the phase boundaries in the liquidus projection of the Mg–Al–Ce phase diagrams that have been reported previously are inconsistent with this study. The hypoeutectic region is smaller compared to the current Mg–Al–Ce phase diagram. In addition, a hexagonal Al₅Ce₂ phase which is isostructural with Al₅La₂ has been identified in these alloys. The research addresses some of the current limitations in understanding the effect of Ce, when added in isolation, on microstructure development in Mg–Al based alloys.

Keywords

Magnesium alloys • Microstructure • Phase diagram

Introduction

In recent years, there has been increasing interest in magnesium alloys due to their low density and high specific strength [1], which are beneficial for vehicle weight reductions and hence improved fuel efficiency. In addition to the commonly used AZ91 and AM50/60 alloy grades, magnesium alloys containing aluminium and rare earth (RE) elements, known as the AE series, have been developed for elevated temperature applications, such as automotive powertrain components, where creep resistance is a major concern. Two notable AE alloys are AE42 (Mg–4Al–2RE) [2] and AE44 (Mg–4Al–4RE) [3]. AE42 exhibits better creep resistance than AZ91 and AM50/60, but it tends to be susceptible to hot tearing during casting [4] and the creep resistance deteriorates rapidly at temperatures above 150 °C [5]. AE44 has improved hot tearing resistance and creep resistance over that of AE42, and has been used for a number of powertrain applications since its first use in a corvette engine cradle [6].

The RE elements used in commercial AE alloys commonly comes from mischmetal, which typically comprises 52–55% cerium (Ce), 23–25% lanthanum (La), 16–20% neodymium (Nd) and 5–6% praseodymium (Pr) [7]. Traditionally, it has been considered that all individual rare earth elements behave similarly in microstructure evolution in AE alloys [8]. In recent years, Nd and Pr prices have increased sharply due to the demand for these elements in magnetic applications. Hence, the abundant La and Ce from mischmetal has become less expensive [9]. As a result, efforts have been made to investigate the effect of individual RE elements in AE alloys. In order to better understand their attributes, such as mechanical properties, castability and creep performance, it is necessary to understand the microstructure and its evolution. However, the observed microstructures are difficult to reconcile with the published phase diagrams. For this reason, the investigation in the present study is focused on the microstructure evolution in
Mg–Al–Ce alloys, and comparisons with the currently available thermodynamic descriptions of the Mg–Al–Ce system.

In this work, the as-cast microstructure of Mg–3Al–10Ce and Mg–4Al–12Ce (all compositions in weight percent unless otherwise specified) alloys were examined and compared with thermodynamic predictions made using the CALPHAD software package Pandat®. The two compositions were chosen because they are located on either side of the α-Mg/Al2Ce phase boundary, as shown in Fig. 1. The aim of the present study is to investigate the accuracy of the existing Mg–Al–Ce phase diagram, particularly the intermetallic phases and the solidification sequence in the current thermodynamic database. These investigations contribute to a better understanding of the microstructure evolution in AE alloys, which may lead to improvements in the thermodynamic database for the Mg–Al–Ce system.

Materials and Methods

The Mg–3Al–10Ce (ACe310) and Mg–4Al–12Ce (ACe412) alloys were prepared from pure elemental magnesium (99.95%), aluminium (99.9%) and cerium (99.5%). The molten magnesium alloys were cast into a wedge mould consisting of two parts: permanent-mould and sand-mould. Molten magnesium and its alloys have a strong tendency to oxidize in air. Hence, the alloys were melted and degased using nitrogen mixed with H134a refrigerant gas. The pouring temperature of the molten metal into the mould was 720 °C and the preheat temperature of the mould was 95 °C. The chemical compositions of the alloys were determined by inductively coupled plasma atomic emission spectroscopy (ICP-OES). The analysed compositions are Mg–3.04Al–10.10Ce for the ACe310 alloy and Mg–3.87Al–12.40Ce for ACe412 alloy.

For microstructural examination of as-cast material, samples were cut from a wedge cast sample, as shown in Fig. 2. The samples were ground to approximately 15 µm using silicon carbide paper with grit size of 500. After grinding, the samples were then polished using cloth with diamond suspension to approximately 0.04 µm particle size. The samples were ultrasonically cleaned for 180 s after each step of grinding and polishing. The solidification microstructure of the prepared samples were analysed using a FEI Quanta 200 scanning electron microscope (SEM), equipped with an Oxford Instruments X-MaxN 20 energy dispersive X-ray (EDX) spectrometer.

Phase identification was performed via X-ray powder diffraction (XRD), using a Bruker D8 diffractometer fitted with CuKα X-ray radiation operated at 40 kV and 40 mA. Data were collected in Bragg-Brentano geometry over the angular range 5–130° 2θ with a scan rate of 2°/min and a step size of 0.02°. The samples were continuously rotated at ~2 Hz during the measurements to improve the particle statistics as much as practical. Whilst this produced accurate relative peak intensities for the intermetallic phases observed in these samples, it did not fully mitigate the effects of the large (for XRD) α-Mg grain size. Therefore, during data analysis the α-Mg phase was modelled using the Pawley method [11] whilst the remaining intermetallic phases were modelled (concurrently) using the Rietveld method [12], as implemented in the Topas software package (version 5, Bruker).

For confirmation, the intermetallic phases in the alloys were also identified using a JEOL 2100F transmission electron microscope (TEM), equipped with an Oxford X-MaxN
The identified intermetallic phases, which can be seen in Fig. 3, have also been further verified by TEM as Al₅Ce₂, Al₂Ce and Mg₁₂Ce. The TEM images are shown in Fig. 4. The TEM analysis confirms that the intermetallic phase with acicular morphology is Al₅Ce₂; the particulate-shaped intermetallic phase is Al₂Ce; the eutectic phase with fine lamellar-like morphology is Mg₁₂Ce.

Discussion

Microstructure Analysis

The lattice parameters of α-Mg were refined to \( a = 3.210 \, \text{Å} \) and \( c = 5.211 \, \text{Å} \) in the XRD analysis, which is in excellent agreement with those commonly reported for pure Mg. The lattice parameters of the newly identified Al₂Ce₂ phase were refined to \( a = 4.605 \, \text{Å} \) and \( c = 3.826 \, \text{Å} \), as shown in Table 1. The refined lattice parameters of this phase are significantly different from the lattice parameters of Al₅La₂ \( (a = 4.478 \, \text{Å} \) and \( c = 3.437 \, \text{Å} \) reported in the literature \([13–15]\). Intermetallic phases such as Al₂Ce and Mg₁₂Ce often have reciprocal substitution of RE elements. This is because the atomic radii, valency and electronegativity of the RE elements in the mischmetal mixture (Ce, La, Pr, Nd) are similar. Therefore, the substitution of lanthanum with cerium, neodymium or praseodymium in the crystal matrix of the Al₅Ce₂, Al₂Ce and Mg₁₂Ce phases is possible based on Hume-Rothery Rules \([17, 18]\). Rzychon and Kielbus \([14]\) indicated that the lattice parameters of Al₅La₂ \((Al₂.12La₀.88)\) phase decrease slightly as small amounts of Ce substitute for La. However, the lattice parameters observed for the pure Al₅Ce₂ in this study are substantially smaller than those reported for Al₅La₂ \([15]\). The reason for this large difference is unclear and is worthy of further investigation.

Previous studies reported that the Al₅La₂ phase has a similar morphology to the Al₂La phase \([14, 17, 19]\). In the present study, Al₅Ce₂ and Al₂Ce have different morphologies; Al₅Ce₂ appears in an acicular morphology and Al₂Ce as a particulate morphology. According to the binary Al–La thermodynamic database, Al₅La₂ is not an equilibrium phase. Rzychon and Kielbus \([14]\) mentioned that the presence of Al₅La₂ phase in the Mg–Al–La alloys is due to two factors: rapid crystallisation and macrosegregation of RE alloying elements. The literature indicates that the metastable Al₅La₂ phase does not develop in slowly cooled gravity cast AE alloys, but develops in fast cooled HPDC AE alloys \([17, 19]\). Interestingly, this phase has been identified in the present study, in which samples were made by gravity die-casting. This is because the geometry of the casting mould also plays a role in developing the cooling profiles.

Another microstructure observation in the SEM images, as shown in Fig. 3b and d, is that some of the particulates are
located within the magnesium grains. EDS and TEM analysis reveals that this particle is Al$_2$Ce phase. The observation of Al$_2$Ce within $\alpha$-Mg grains suggests that Al$_2$Ce may act as a nucleant during solidification, which is in agreement with the results of previous studies [20–22].

Phase Diagram Evaluation

Computational thermodynamics of magnesium alloy systems have been utilised in industry to accelerate design and optimisation of alloys. In the present study, the thermodynamic database of the Mg–Al–Ce system was taken from the PanMg 2017 [10] database using Pandat. In this study, the comparison between the identified phases of the investigated alloys using ex situ characterisation methods with the existing Mg–Al–Ce phase diagram can be used to verify and improve the database for this system.

XRD and TEM analysis reveals that the phases present in ACe310 and ACe412 alloys are $\alpha$-Mg, Al$_5$Ce$_2$, Al$_2$Ce and Mg$_{12}$Ce. By comparing with the Mg–Al–Ce phase diagram and the Scheil-Gulliver solidification simulation, shown in Figs. 1 and 5 respectively, the phases identified in both the ACe310 and ACe412 alloys do not match the phases predicted in the thermodynamic database. Only the identified Al$_2$Ce phase matches with the Scheil-Gulliver prediction, but not Mg$_{12}$Ce and Al$_5$Ce. In addition, there is no Al$_{11}$Ce$_3$ phase observed in ACe412 alloy in the present study. It is worth mentioning that the Al$_5$Ce$_2$ phase is not an equilibrium phase based on the binary Al-RE thermodynamic

Fig. 3 XRD analysis on a ACe310 alloy and c ACe412 alloy, the calculated patterns are represented in red and the experimental patterns represented in blue. The difference between the experimental and calculated patterns is represented in grey. SEM image on b ACe310 alloy and d ACe412 alloy.
database. However, it is interesting to note that the metastable Al\textsubscript{5}La\textsubscript{2} phase can be shown in the equivalent Mg–Al–La phase diagram by suppressing the thermodynamically stable Al\textsubscript{2}La phase in Pandat.

It is interesting that the Al\textsubscript{2}Ce particles in both the ACe310 and ACe412 alloys are located within the magnesium grains, as shown in Fig. 3b and d. This indicates that the Al\textsubscript{2}Ce phase is probably the primary phase developed in these alloys, even though the predicted primary phase in ACe310 alloy is the α-Mg phase, as shown in Fig. 1. In this case, the invariant point, phase boundaries and the predicted solidification pathway projected onto the liquidus phase diagram, as shown in Fig. 1, are inconsistent with the experimental results suggesting that the thermodynamic database for Mg–Al–Ce needs to be further refined.

Table 1 Space group and refined lattice parameters for phases identified in ACe310 alloy (the lattice parameters for the ACe412 alloy refined to similar values)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Refined lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Mg</td>
<td>P6\textsubscript{3}mmc</td>
<td>a 3.210  c 5.211</td>
</tr>
<tr>
<td>Mg\textsubscript{12}Ce</td>
<td>I4/mmm</td>
<td>a 10.316  c 5.943</td>
</tr>
<tr>
<td>Al\textsubscript{2}Ce</td>
<td>Fd-3 m</td>
<td>a 8.086  c –</td>
</tr>
<tr>
<td>Al\textsubscript{5}Ce\textsubscript{2}</td>
<td>P6/mmm</td>
<td>a 4.605  c 3.826</td>
</tr>
</tbody>
</table>

**Fig. 4** TEM image, micro beam electron diffractions and EDX spectra showing the microstructure and identification of intermetallic phases in as-cast ACe310 alloy. (a) and (b) the acicular intermetallic phase was identified as Al\textsubscript{5}Ce\textsubscript{2}, (c) and (d) the particulate-shaped intermetallic phase was identified as Al\textsubscript{2}Ce, (e) and (f) the lamellar-like intermetallic was identified as Mg\textsubscript{12}Ce.
Conclusions

In present study, the identified phases of ACe310 and ACe412 alloys are α-Mg, Al5Ce2, Al2Ce and Mg12Ce. The intermetallic phase, Al5Ce2, develops an acicular morphology. The lattice parameters of this phase are significantly different from the Al5La2 phase reported in the literature. In addition, Al5Ce2 phase has not been reported in the open literature and it is currently not listed in the crystallographic database. Lastly, the phases identified in the ACe310 alloy are inconsistent with the Scheil-Gulliver predictions from PanMg 2017 thermodynamic database. The present study shows that ACe310 alloy is a hyper-eutectic alloy. The magnesium database and Pandat simulation are indeed very useful for both research and industrial purposes. However, further research is certainly required to improve the database for greater accuracy of thermodynamic predictions in the Mg–Al–Ce system.

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Chapter 5

(Al,Mg)₃La: a new phase in the Mg-Al-La system

Chapter 5

(Al,Mg)₃La: a new phase in the Mg-Al-La system

Charlotte Wong¹, Mark J. Styles², Suming Zhu¹, Dong Qiu¹, Stuart D. McDonald³, Yuman Zhu¹, Mark A. Gibson¹,²,⁴, Trevor B. Abbott⁵, Mark A. Easton¹

¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia

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(Al,Mg)$_3$La: a new phase in the Mg–Al–La system

Charlotte Wong,$^a$ Mark J. Styles,$^{b,*}$ Suming Zhu,$^a$ Dong Qiu,$^a$ Stuart D. McDonald,$^c$
Yuman Zhu,$^d$ Mark A. Gibson,$^{a,b,d}$ Trevor B. Abbott$^e$ and Mark A. Easton$^a$

$^a$School of Engineering, RMIT University, Carlton, Victoria 3053, Australia, $^b$CSIRO Manufacturing, CSIRO, Clayton, Victoria 3168, Australia, $^c$School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia, $^d$Department of Materials Science and Engineering, Monash University, Victoria, 3800, Australia, and $^e$Magontec Ltd, Sydney, New South Wales 2000, Australia. *Correspondence e-mail: mark.styles@csiro.au

During an investigation of the Mg-rich end of the Mg–Al–La system, a new ternary phase with the composition of (Al,Mg)$_3$La was identified. The crystal structure of this phase was determined by conventional X-ray powder diffraction and transmission electron microscopy analysis and refined using high-resolution X-ray powder diffraction. The (Al,Mg)$_3$La phase is found to have an orthorhombic structure with a space group of $C222_1$ and lattice parameters of $a = 4.3365$ (1) Å, $b = 18.8674$ (4) Å and $c = 4.4242$ (1) Å, which is distinctly different from the binary Al$_3$La phase ($P6_3/mmc$). The resolved structure of the (Al,Mg)$_3$La phase is further verified by high-angle annular dark-field scanning transmission electron microscopy.

1. Introduction

The high specific strength of magnesium alloys makes them attractive for use in transport applications where weight savings are important. However, the most common magnesium alloys such as AZ91 (Mg–9Al–1Zn) and AM60 (Mg–6Al–0.3Mn) tend to suffer from poor creep resistance, limiting their use in high-temperature environments (Luo, 2004). Alloys based on the Mg–Al–RE systems are found to have not only improved high-temperature creep resistance, but also a good balance of room-temperature mechanical properties (Zhu et al., 2015), which leads to their being used in transport applications. The effects of individual rare-earth elements such as La and Ce on microstructure evolution and phase formation in Mg–Al alloys are poorly understood at present. Recent investigations by the authors on the Mg-rich end of the Mg–Al–La system have revealed some significant shortcomings in the published phase diagrams. In particular, the microstructures observed are often inconsistent with those predicted by solidification models based on the current thermodynamic databases.

Binary Al–La, Al–Mg and La–Mg phase diagrams have been developed and evaluated in the past (Zhou & Napolitano, 2006; Guo & Du, 2004; Liang et al., 1998; Saunders, 1990; Yin et al., 2000; Cacciamani & Ferro, 2001; Ansara et al., 1997). The ternary Mg–Al–La phase diagram was first published based on experimental data collected prior to 1988 (Rogl, 1988). A partial isothermal section at 400°C for La concentrations up to 33.3 at. % was developed by Zarechnyuk et al. (1981). Following this, Odinaev et al. (1988) prepared and investigated 115 alloys, annealing them at 400°C for 480 h to develop an understanding of the phase equilibria at this temperature. The system was further investigated and
reviewed by Raghavan (2008). Recently, Hosseinifar & Malakhov (2010) studied two key alloys in the Mg–Al–La system and optimized the Mg–Al–La ternary phase diagrams. The Mg–Al–La thermodynamic database was also systematically evaluated and optimized by Jin et al. (2013). Table 1 summarizes the equilibrium solid phases currently reported in the Mg–Al–La system. It is worth mentioning that the individual RE elements, such as La and Ce, are often found to substitute within the Al–RE and Mg–RE intermetallic phases (Rzychon et al., 2013; Kleber et al., 1970). For example, it is known that Al$_{12}$La$_3$ and Al$_{11}$Ce$_3$ are isostructural.

The research to date has tended to focus on commercial ‘AE’ magnesium alloys (A = Al, E = rare earth). Previous studies (Bai et al., 2012; Zhu et al., 2016) on AE alloys with lanthanum as the rare-earth element indicated that the main intermetallic phase is Al$_{12}$La$_3$ followed by Al$_3$La. In order to understand the discrepancies between the predicted and observed microstructures in Mg–Al–La alloys, a more detailed phase identification was performed using X-ray diffraction (XRD) and transmission electron microscopy (TEM). During this study, it was found that the main intermetallic phase in these alloys did not match the structures of the Al–RE phases commonly reported in these alloys, which are expected to be Al$_{12}$La$_3$ (Gomes de Mesquita & Buschow, 1967), Al$_3$La (Havinga, 1975) and Al$_3$La (Rao et al., 1982). Here, we present the results of the characterization of a previously unreported intermetallic phase found in an Mg–4.5Al–6.3La alloy. The implications for understanding the microstructural evolution in AE alloys during solidification will be discussed elsewhere.

2. Experimental procedure

2.1. Material preparation

An alloy with composition Mg–4.5Al–6.3La (wt%) was prepared from 99.9% pure Mg and Al, and 99.5% pure La by melting in an electric resistance furnace using a boron-nitride-coated stainless steel crucible. An inert cover gas was used to protect the sample from oxidation during melting. The composition of the sample was measured using inductively coupled plasma–atomic emission spectroscopy and the results are given in Table 2.

2.2. X-ray powder diffraction

Conventional XRD data were collected from a polished cross-section of the as-cast ingot using a Bruker D8 diffractometer fitted with a Cu X-ray tube (\(\lambda = 1.54059\) Å). Data were collected between 5 and 140° 2θ using standard Bragg–Brentano geometry (Klug & Alexander, 1975) and a small linear strip detector. The flat plate sample was spun at \(\sim 2\) Hz in order to improve the particle statistics as much as possible.

High-resolution XRD patterns were collected using the Powder Diffraction beamline (Wallwork et al., 2007) at the Australian Synchrotron. For the synchrotron data collection, a small amount of powder was filed from the as-cast alloy and sieved to obtain particles less than 75 µm in size. This powder was encapsulated in a glass ampoule under argon and annealed at \(350^\circ\)C for 2 h to relieve the stresses induced by filing. The powdered samples were packed into glass capillaries and studied in Debye–Scherrer geometry (Klug & Alexander, 1975). A monochromatic X-ray beam with a nominal energy of 18 keV was used and data were collected over the angular range 2–82.5° 2θ using the Mythen curved position-sensitive detector (Bergamaschi et al., 2010). The capillaries were continuously rotated about their axes at \(\sim 1\) Hz during the measurement. A precise determination of the X-ray wavelength (\(\lambda = 0.68861\) Å) was derived from diffraction patterns collected from a sample of LaB$_6$ (NIST SRM 660b). The diffraction patterns, which were acquired in pairs with the detector offset by 0.5° 2θ, were merged using the program CONV2AS (Rowles, 2010) in order to eliminate the gaps between the modules of the Mythen detector. The resulting merged data were then analysed by the Rietveld method (Rietveld, 1969), as implemented in the software package TOPAS (version 5, Bruker, 2014).

2.3. Electron microscopy

For microstructural examination a thin sample was cut from the cast ingot, mounted in epoxy resin and ground to approximately 15 µm. After grinding, the samples were then polished using cloth with diamond suspension to approximately 0.04 µm particle size. The samples were ultrasonically...
cleaned between each step of grinding and polishing. The as-cast microstructure of each prepared sample was analysed using a Hitachi TM3030 scanning electron microscope (SEM) operating at 15 kV with a backscattered electron detector.

For TEM examinations, discs of 3 mm diameter and 0.1 mm thickness were cut from the bulk sample and ground, followed by low-angle ion milling using a Gatan Precision Ion Polishing System (PIPS). The TEM foils were examined in a Tecnai G2 T20 microscope, equipped with a Bruker Quantax 200 energy-dispersive X-ray (EDX) system. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was conducted in a double-corrected FEI Titan 300-300 FEGTEM microscope operated at 300 kV. A 15 mrad convergence semi-angle was used, corresponding to a STEM resolution of 0.12 nm. HAADF-STEM images were acquired with the camera length set to give a collection semi-angle of 57–200 mrad. For better interpretability, raw HAADF-STEM images were processed by masking diffraction spots in the fast Fourier transforms of the original images and then back-transforming using the Gatan DigitalMicrograph software package.

3. Results and discussion

A typical SEM image and the conventional XRD data collected from the bulk sample of the Mg–4.5Al–6.3La alloy are shown in Fig. 1. The SEM image (Fig. 1a) reveals that the microstructure consists of primary α-Mg dendrites surrounded by a eutectic of α-Mg and intermetallic phase. For the XRD data (Fig. 1b), the peaks corresponding to the α-Mg phase can be readily identified; however, the observed intensities are not well modelled by the corresponding crystal structure. This is due to the poor particle statistics resulting from the large α-Mg dendrites present in the as-cast microstructure (Fig. 1a).

Besides the α-Mg phase, the remaining peaks in this data set could not be satisfactorily identified using the International Centre for Diffraction Data PDF-4+ database (ICDD, 2017) or matched with other phases reported in the literature for Mg–Al–RE systems (Table 1).

The remaining peaks in the conventional XRD data were assumed to be from the same unknown phase and were indexed using the LSI method implemented in TOPAS. Several orthorhombic space groups matched the observed peaks well; however, taking into account systematic absences, several orthorhombic space groups matched the observed indexed using the LSI method implemented in TOPAS.

Figure 1
(a) SEM image from a bulk sample of the Mg–4.5Al–6.3La alloy. The microstructure consists of two phases, α-Mg (dark contrast) and a previously unreported La-containing intermetallic phase (bright contrast). (b) The corresponding XRD data have been fitted using the Pawley (1981) method. The intermetallic phase has an orthorhombic (C222) structure with lattice parameters a = 4.34, b = 18.96 and c = 4.43 Å. The observed, calculated and difference patterns are shown in Fig. 1(b). All of the observed peaks were accounted for using this method, suggesting that the sample is indeed composed of two phases without additional impurity phases.

TEM data were collected from samples of the as-cast Mg–4.5Al–6.3La ingot in order to determine the composition of the intermetallic phase and corroborate the space group identified using the XRD data. The low-magnification bright-field image, given in Fig. 2(a) shows a large number of intermetallic particles embedded on the α-Mg grains. EDX spot analyses performed on these particles indicate that the composition of the intermetallic phase is close to (Al,Mg)3La (e.g. Fig. 2b). The analysed particles were carefully selected to minimize the contribution of the Mg matrix and it is thought that the presence of a small amount of Mg in this phase is genuine, although it is difficult to quantify the Mg fraction precisely (the effects of Mg concentration on the structure of Al3La will be the subject of a future investigation). Selected area diffraction (SAED) data were collected from the intermetallic particles and the results are shown in Fig. 2(c). Indexing of the SAED patterns and measuring of tilting angles between the common zone axes confirm that the intermetallic phase has an orthorhombic space group with lattice parameters a = 4.34, b = 18.87 and c = 4.42 Å, in excellent agreement with the XRD data. It should be noted that there are reflections at the positions of (001), l = 2n + 1, as a result of double diffraction. For example, the (001) spot can be produced by double diffraction from (021) and (020).
A preliminary structure determination was attempted using the conventional XRD data. Based on the TEM EDX results, a simplified composition of Al$_3$La was assumed due to the low X-ray scattering contrast between Al and Mg. The density of similar phases reported in the literature (e.g. Al$_3$La and Al$_{11}$La$_3$) range between 3.95 and 4.20 g cm$^{-3}$. Based on the unit cell volume and chemistry observed, it was determined that there should be four formula units per unit cell to give a density of $\sim$4.01 g cm$^{-3}$. Using this information, a structure determination was attempted using the simulated annealing method (Coelho, 2000). Four unique atomic sites were used, with one La atom and three Al atoms. In order to help identify special positions within the crystal structure, occupancy merge radii for the Al atoms of 1.0 Å and anti-bump radii of 3.0 and 3.3 Å for Al–La and Al–Al atom pairs, respectively, were used. Other refinable parameters, such as lattice parameters and background function for example, were fixed during the simulated annealing.

After several iterations it became apparent that the $x$ and $z$ coordinates of all four sites quickly converged on the special positions 0 and $\frac{1}{4}$, respectively (4$b$ site), giving densities close to the target 4.01 g cm$^{-3}$. These coordinates were fixed in subsequent refinements, with only the $y$ coordinate for each atom allowed to refine. This process resulted in a preliminary set of atomic coordinates of $y = 0.10, 0.47, 0.33$ and 0.75 for the La, Al1, Al2 and Al3 sites, respectively. However, due to the poor particle statistics evident in the $\alpha$-Mg phase, the accuracy of this proposed structure was unclear.

To improve the reliability of the structure refinement, synchrotron data were collected from a powdered sample that had been annealed under argon to relieve stresses induced by the grinding process. The results from the synchrotron measurement are shown in Fig. 3. The particle statistics from the Mg phase were improved considerably, allowing the peak intensities to be accurately modelled using the Rietveld method. In addition to the (Al,Mg)$_3$La phase of interest, a small amount ($\sim$2 wt%) of magnesium oxide (MgO) was present.

![Figure 2](image1.png)

Figure 2
(a) TEM bright-field image, (b) EDX analysis and (c) a series of selected area diffraction patterns of the intermetallic phase in the Mg–4.5Al–6.3La alloy. The EDX spectrum suggested a composition close to (Al,Mg)$_3$La. The diffraction patterns could be well indexed according to the orthorhombic (C$2\overline{2}$2$_1$) structure with lattice parameters $a = 4.34$ Å, $b = 18.96$ Å and $c = 4.43$ Å. The experimental tilting angles are close to those calculated (numbers in brackets).

![Figure 3](image2.png)

Figure 3
(a) Final fit to the synchrotron data for the powdered sample of Mg–4.5Al–6.3La. The observed, calculated and difference patterns are shown in blue, red and grey, respectively. (b) Enlargement of a preliminary refinement highlighting anisotropic broadening of the (Al,Mg)$_3$La phase peaks ($R_{wp} = 3.61\%$). (c) Improvement achieved in final fit using the Stephens (1999) method to model the anisotropic broadening ($R_{wp} = 3.05\%$).
Table 3
Crystallographic parameters refined for the (Al,Mg)₃La phase.

The uncertainties reported in brackets are 2× the estimated standard deviations (i.e. 2σ) calculated by TOPAS.

<table>
<thead>
<tr>
<th>Formula</th>
<th>Density (g cm⁻³)</th>
<th>Lattice parameters a, b, c (Å)</th>
<th>Volume (Å³)</th>
<th>Space group</th>
</tr>
</thead>
<tbody>
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<td>(Al,Mg)₃La</td>
<td>4.0342 (1)</td>
<td>4.3365 (1), 18.8674 (4), 4.4242 (1)</td>
<td>361.98 (1)</td>
<td>C222,</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atomic coordinates</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Occupancy</th>
<th>Bombok (Å²)</th>
</tr>
</thead>
<tbody>
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<td>La</td>
<td>0</td>
<td>0.1043 (1)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.70 (3)</td>
</tr>
<tr>
<td>Al1</td>
<td>0</td>
<td>0.4666 (4)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.9 (2)</td>
</tr>
<tr>
<td>Al2</td>
<td>0</td>
<td>0.3342 (4)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.9 (2)</td>
</tr>
<tr>
<td>Al3</td>
<td>0</td>
<td>0.7493 (4)</td>
<td>0.25</td>
<td>1.0</td>
<td>0.7 (2)</td>
</tr>
</tbody>
</table>

detected as a result of the annealing processes. The sample was also found to contain a very small fraction of the Al₁₁La₃ phase as well as a cubic phase with a structure similar to a mixed La–Ce oxide or La hydride (Fm̅3m, a = 5.61 Å) (Korst & Warf, 1966; Sung Bae et al., 2004). A trace amount of f.c.c.
Al was detected, which is likely to be an impurity introduced during powder preparation.

The simulated annealing procedure described above was repeated for the synchrotron data, giving results in excellent agreement with the laboratory data. The final crystal structure parameters refined from the synchrotron data (using the Rietveld method) are given in Table 3 and a three-dimensional view of the crystal structure is given in Fig. 4. It should be noted that the high resolution of the synchrotron data also revealed a small amount of anisotropic broadening of the (Al,Mg)₃La phase peaks, as highlighted in Fig. 3(b). In the final Rietveld analysis, the (Al,Mg)₃La peak shapes were described using the Stephens (1999) method, which describes anisotropic microstrain broadening. This approach improved the quality of fit, as highlighted in Fig. 3(c), but did not significantly change the refined atomic coordinates. Anisotropic microstrain could indicate the presence of defects within the (Al,Mg)₃La crystallites, or the effects of lattice mismatch between (Al,Mg)₃La and the α-Mg matrix. Alternatively, the anisotropic broadening could be due to the plate-like morphology of the small eutectic particles (i.e. anisotropic crystalline size broadening). The data do not support a detailed peak profile analysis and further work is required to elucidate this point.

The crystal structure consists of La atoms coordinated with 14 Al(Mg) atoms, 12 of which are arranged in two hexagonal rings with plane normals aligned parallel to the a-axis of the unit cell. The two remaining Al atoms lie in the same plane (bc) as the La atom. This Al(Mg) atom packing arrangement is consistent with other Al-La intermetallic phases such as Al₁₁La₃. The Al–La interatomic distances range from 3.31 to 3.53 Å, which is significantly larger than in the hexagonal Al₁₃La phase (2.98–3.32 Å, Ni₃Sn-type structure) and more similar to that observed in the Al₁₁La₃ phase (3.27–3.78 Å). The incorporation of a low concentration of Mg atoms into the (Al,Mg)₃La phase may account for the slightly larger Al(Mg) to La distances, compared with Al₁₁La₃, due to the larger radius of Mg relative to Al. The Al–Al and La–La interatomic distances are in the ranges 2.51–3.10 Å and 4.34–4.52 Å, respectively, which also compares well with the distances observed in Al₁₁La and Al₁₃La₃.

The proposed structure was verified by atomic scale HAADF-STEM imaging, shown in Fig. 5. In Figs. 5(c) and 5(d), each bright dot represents a column rich in La atoms because the intensity of HAADF-STEM imaging is approximately proportional to the square of the atomic number (Pennycook & Jesson, 1992) (the atomic number is 12 for Mg, 13 for Al and 57 for La). The Al(Mg) atoms are also detected around the much brighter La atoms, but with weaker contrast. Needless to say, it is impossible to distinguish Al atoms from Mg atoms in the HAADF-STEM images. The atom arrangements viewed along these two directions are consistent with those in the proposed structure shown in Figs. 5(a) and 5(b).

Lastly, samples of this alloy were heat treated at 350°C for 500 h and at 500°C for 100 h to investigate the thermal stability of the (Al,Mg)₃La phase. Conventional XRD data and SEM data collected from these samples also showed two-
phase microstructures consisting of α-Mg and (Al,Mg)₃La, indicating that (Al,Mg)₃La is an equilibrium phase in the Mg–Al–La system.

4. Conclusions

A new intermetallic phase has been identified in the Mg–Al–La system, which has the composition of (Al,Mg)₃La. The crystal structure has been resolved using high-resolution synchrotron X-ray powder diffraction to be orthorhombic with space group C222₁ and lattice parameters \( a = 4.3365 \) Å, \( b = 18.8674 \) Å, and \( c = 4.4242 \) Å. The resolved unit-cell parameters and atom occupancy have been verified by HAADF-STEM imaging and there is an excellent agreement between the two techniques. The Al(Mg) atom packing arrangements of the (Al,Mg)₃La phase are consistent with those of the other Al–La intermetallic phases such as Al₁₂La₃.

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References


Chapter 6

Solidification path and microstructure evolution of Mg-3Al-14La alloy: implications for the Mg-rich corner of the Mg-Al-La phase diagram

Charlotte Wong¹, Kazuhiro Nogita³, Mark J. Styles², Suming Zhu¹,⁴, Dong Qiu¹, Stuart D. McDonald³, Mark A. Gibson¹,²,⁴, Trevor B. Abbott¹,⁴,⁵, Mark A. Easton¹

¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia

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Solidification path and microstructure evolution of Mg-3Al-14La alloy: Implications for the Mg-rich corner of the Mg-Al-La phase diagram

Charlotte Wong a, Kazuhiro Nogita b, Mark J. Styles c, Suming Zhua a, d, Dong Qiua, Stuart D. McDonaldb, Mark A. Gibsona, c, d, Trevor B. Abbott e, Mark A. Easton a, *

a School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
b School of Mechanical and Mining Engineering, The University of Queensland, Brisbane, Queensland 4072, Australia
c CSIRO Manufacturing, Clayton, Victoria 3168 Australia
d Department of Materials Science and Engineering, Monash University, Clayton, Victoria 3800, Australia
e Magontec Ltd, Sydney, New South Wales 2000, Australia

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A B S T R A C T

The solidification path and microstructure evolution in Mg-3Al-14La alloy have been investigated by in-situ synchrotron radiography, thermal analysis and characterisation of the final microstructure. It is shown that the solidification sequence begins with the precipitation of primary Al5La2, followed by a eutectic with the products z-Mg+Al5La2, then a mono-variant binary eutectic with the products z-Mg+Mg12La and lastly a ternary eutectic with the products z-Mg+(AlMg)13La. This solidification sequence is found to be significantly different to the current Mg-Al-La thermodynamic description. The two main discrepancies are: (i) with Al5La2 being the primary phase, the Mg-3Al-14La alloy is a hyper-eutectic alloy rather than a hypo-eutectic alloy as currently described and (ii) the (AlMg)13La phase, which was recently identified as a new phase in the Mg-Al-La system, is also present in the Mg-3Al-14La alloy. The results from this study will be useful for the improvement of the current thermodynamic description of the Mg-Al-La system.

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1. Introduction

The high specific strength and good castability of magnesium alloys facilitate their use in automotive and other transport applications where weight savings can lead to improved fuel efficiency [1]. The most commonly used Mg alloys are those based on the Mg-Al system, such as AZ91, AM50 and AM60, which have good mechanical properties, good castability and low cost [2–4]. However, these alloys do not possess good elevated temperature properties, which limits their application [3]. Mg-Al-RE based alloys are well known to have improved creep resistance [3,5,6], which is important for powertrain applications [7] in the automotive industry. Mg-Al-RE alloys also show excellent castability [8] and a good combination of strength and ductility, particularly after aging [9].

Historically, rare earth (RE) elements were added to Mg-Al-RE alloys in the form of Ce-rich mischmetal, comprised of 52–55% cerium (Ce), 23–25% lanthanum (La), 16–20% neodymium (Nd) and 5–6% praseodymium (Pr) [7,10,11]. In recent years, there has been an increase in the demand for Nd in applications such as permanent magnets [10]. The demand for Nd and other less common RE elements has caused the cost of mischmetal to increase substantially, while the more abundant Ce and La have become less expensive [10] making these elements preferable alloying additions for Mg-Al-RE alloys. Recent investigations have indicated that the addition of individual RE elements, such as La and Ce, to Mg-Al-RE alloys can lead to the development of different constituents in the microstructure and there is some debate about whether this leads to different mechanical properties [12–14]. However, the solidification paths that lead to the formation of the different microstructures in the ternary Mg-Al-La and Mg-Al-Ce systems are not well understood.

Equilibrium phase diagrams provide the thermodynamic data for the prediction of phase evolution during solidification [15]. Currently, this information is limited for Mg-Al-RE alloys. For example, previous studies of the Mg-Al-La and Mg-Al-Ce systems show inconsistent liquidus temperatures [16–19]. There is even debate about the liquidus line for Al5Ce and Al13Ce3 between

* Corresponding author.
E-mail address: mark.easton@rmit.edu.au (M.A. Easton).

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different experimental studies in the Mg-rich corner of the phase diagram [17,18]. Similarly, a study on the Al-Mg-La system [19] reported higher ternary liquidus temperatures than what had been reported previously, although this study focused entirely on the Al-rich corner. In addition, our recent investigations showed inconsistencies between microstructural observations and thermodynamic predictions in the Mg-Al-Ce system [20], providing further motivation for investigation into the Mg-Al-La system.

The present study aims to investigate the solidification process and microstructure evolution in a Mg-3Al-14La alloy. Solidification pathways are typically inferred from microstructural observations made ex-situ at room temperature [5,7,10,21–25], sometimes leading to an ambiguous interpretation of the results [26,27]. In-situ methods, such as time-resolved synchrotron radiography, can provide direct evidence for microstructural evolution and solidification pathways [26,28,29]. In the present work, in-situ observations of the microstructure evolution during solidification are combined with ex-situ investigations of the as-cast microstructure, thermal analysis and thermodynamic predictions to understand the solidification sequence of the Mg-3Al-14La alloy. The information gained from this study can be used for improving the Mg-Al-La phase diagram and its database.

2. Methodology

2.1. Alloy preparation

The Mg-3Al-14La (weight per cent, termed as ALa314) alloy was prepared from pure elemental magnesium (99.95%), aluminium (99.9%) and lanthanum (99.9%) by sand casting. The alloy materials were melted under nitrogen mixed with HFC134A refrigerant gas. After holding at 720 °C for approximately 20 min, the molten metal was poured into the mould which was at a temperature of 95 °C (after preheating to above 100 °C) to remove moisture from the mould. The chemical composition of the alloy was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table 1).

2.2. In-situ synchrotron radiography

In-situ synchrotron radio-tomography experiments were performed on the ALa314 alloy at the Spring-8 synchrotron in Hyogo, Japan (beamline BL20B2). The sample was cut and polished to 9 mm in length, 9 mm in width and 150 μm in thickness. The sample size was selected to fit a specially designed heating stage with a MgO frame used to contain the alloy [30]. The sample was placed at a location where it could be exposed to the synchrotron X-ray beam during both the heating and cooling cycles. A monochromatic X-ray beam with 13 keV photon energy was used in this experiment. A thermocouple was placed inside the furnace directly next to the sample and the sample holder. The furnace was gradually heated to 680 °C at 0.5 °C/s (32.5 °C/min) in a confined furnace with visual observation indicating a fully molten sample. The molten alloy was cooled at a controlled rate of 0.08 °C/s (5 °C/min) down to 550 °C, observing the solidification process. Because the heating unit was located above the field of view (FoV) and the thermocouple was located outside the MgO plates, the imposed thermal gradient led to a temperature difference across the FoV, with the hotter part at the top of the sample compared to the cooler part at the bottom of the sample. The details of the selection of sample thickness, the principle of photon energy selection and the experimental setup are explained elsewhere [30].

It is important to have a slow cooling rate to ensure that every step of the microstructure evolution is captured during the image acquisition. During the heating and cooling processes, the transmitted beam was detected and recorded at a rate of 1 frame per second. In the location where solidification starts, the physical size of the sample (9 mm × 9 mm) is larger than the FoV of the X-ray beam (5 mm × 5 mm). The pixel size was 2.74 μm/pixel. Image processing and analysis were performed using a specially written script via the Windows command prompt and ImageJ [31].

2.3. Thermal analysis

A boron nitride coated steel cup with an outer diameter of 35 mm at the top and 22 mm at the bottom, a height of 40 mm and a uniform wall thickness of 3 mm was used to melt and solidify the alloy during the thermal analysis experiment. A K-type mineral insulated metal sheathed (MIMS) thermocouple was placed inside the centre of the casting at a distance of 20 mm from the base of the steel cup. The hot junction area of the thermocouple was protected by an additional external fitted steel tube. Consequently, the same thermocouple was used throughout the experiments without the need to re-melt the sample between analyses. Cover gas (1% SF6 in CO2) was used throughout the experiment to protect the samples from oxidation. The thermocouple was calibrated using the melting point of pure aluminium (660 °C) as the reference. The variation of the arrests was found to be within ±0.3 °C as a 95% confidence interval. The alloy solidified with a cooling rate of 0.6 °C/s. During solidification, the temperature data was collected every 0.15 s. Three thermal analysis cycles for the ALa314 alloy were carried out. The phase transformation temperatures were determined from the first derivative of the measured cooling curves.

2.4. Microstructure characterisation

For microstructural examination, the as-cast sample and the solidified sample from the in-situ synchrotron experiment were first ground using silicon carbide paper to a grit size of 500. The samples were then polished with diamond and finished with alumina suspension with approximately 0.04 μm particle size. The samples were ultrasonically cleaned in ethanol for 180 s after each step of grinding and polishing. The microstructure of these samples was analysed using an FEI Versius 460L scanning electron microscope (SEM), equipped with an Oxford Instruments X-MaxN energy dispersive X-ray spectrometer (EDS) at 3 kV.

To identify the phases in the as-cast sample, X-ray powder diffraction (XRD) data were collected from the polished sections using a Bruker D8 diffractometer equipped with a Cu X-ray tube operated at 40 kV and 40 mA. XRD data were collected over the range 5–130° 2θ with a scan rate of 2°/min and a step size of 0.02° using a small linear position sensitive detector. The acquired XRD patterns were analysed using a combination of the Rietveld method [32] and Pawley method [33] through the Topas software package.

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Mg</th>
<th>Al</th>
<th>La</th>
<th>Zn</th>
<th>Cu</th>
<th>Fe</th>
<th>Mn</th>
<th>Ni</th>
<th>Be</th>
<th>Ce</th>
<th>Gd</th>
<th>Nd</th>
<th>Pr</th>
<th>Si</th>
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<tbody>
<tr>
<td>ALa314 Bal.</td>
<td>3.2</td>
<td>14.4</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.02</td>
<td>0.01</td>
<td>0.01</td>
<td>&lt;0.001</td>
<td>0.01</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>&lt;0.005</td>
<td>0.02</td>
<td></td>
</tr>
</tbody>
</table>
The structure models for α-Mg, Al212La0.88 (Al5La2), (AlSi)5La2 and Mg12La phases present in the alloy were taken from Pearson’s handbook [34] and the International Centre for Diffraction Data (ICDD) PDF-4+ database [35], whereas the structure model for the (Al,Mg)3La phase was taken from the current authors work [36]. A JEOL 2100F transmission electron microscope (TEM), equipped with an Oxford X-MaxN 80T EDX spectrometer was used to further identify individual intermetallic phases in the alloy. The TEM foils were prepared by a Gatan Precision Ion Polishing System (PIPS) at 4 keV with an incident angle of 4°.

The characterised phases in the as-cast sample, thermal analysis data and the real-time solidification sequence were compared with those predicted by the Lever and the Scheil-Gulliver equations using Pandat® and the PanMagnesium 2018 database [37]. The combination of SEM micrographs, ex-situ phase characterisation and in-situ synchrotron radiography was used to determine the primary phase solidification region.

3. Results

3.1. In-situ synchrotron radiography

The results of the in-situ synchrotron radiography experiment are shown as a time series of images (Fig. 1), capturing various points in the solidification sequence while cooling at a rate of 5 °C/min. The video from which these images have been extracted can be viewed online (insert online link). The brighter contrast represents the α-Mg dendrites, whereas the intermetallic phases are darker in contrast due to the difference in atomic number that affects the X-ray attenuation. During solidification, dark intermetallic phase particles start to form at a furnace temperature of 662 °C although the furnace temperature dropped to 637 °C before significant numbers of these particles were observed (Reaction 1, Fig. 1b), then dendrites form sometimes on the intermetallic particles at a furnace temperature of 597 °C with continued formation or coarsening of the dark intermetallic phase (Reaction 2, Fig. 1c), and finally another eutectic phase forms at a furnace temperature of 590 °C (Reaction 3, Fig. 1d). It should be emphasised that the temperatures quoted are furnace temperatures, not the temperature of the sample, which will be significantly higher as the sample is held between two insulating MgO plates.

3.2. Thermal analysis

The cooling curves and their first derivative curves obtained from the thermal analysis are shown in Fig. 2. Three repeats of the temperature data were collected. Fig. 2 shows that the AlLa314 alloy exhibits a narrow range of solidification, with four exothermic peaks corresponding to solidification reactions observed over the range 630 °C to 600 °C. Whilst not completely clear, there appears to be a small reaction around 630 °C (Reaction 1) as seen by the increase in slope. There is a strong peak around 617 °C (Reaction 2), with another peak very close to it at approximately 609 °C (Reaction 3). There also appears to be an additional reaction at approximately 602 °C (Reaction 4). It should be noted that while the sequence of reactions matches with synchrotron observations, the temperatures are generally higher than those recorded from the synchrotron furnace temperatures particularly as solidification continued, whilst the initial reaction which is difficult to detect in both the in-situ observation and thermal analysis is similar. Thermal analysis obtains more reliable measurements of temperature.

Fig. 1. In-situ synchrotron radiography shows the solidification and microstructure evolution in the time sequence, showing 4 stages of solidification (a) fully liquid, (b) Reaction 1 where intermetallic particles form, (c) Reaction 2 where α-Mg dendrites form and (d) the formation of eutectic between dendrites. The red circles represent the first appearance of the intermetallic particles in each time frame, and the black circles represent the existing intermetallic particles retained from the previous time frame. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)
for the phase transitions, as the thermocouples are placed directly in the solidifying melt instead of in the furnace outside the insulating MgO plates as in the synchrotron observations.

### 3.3. Phase identification in the as-cast microstructure

Five different phase morphologies were observed in the microstructure of the alloy cast into the mould. These included equiaxed dendritic grains, polyhedral and acicular particles within the dendritic grains, a fine lamellar eutectic and brighter blocky eutectic particles (Fig. 3a). A similar microstructure was observed in the solidified sample from the in-situ synchrotron experiment (Fig. 3b). The polyhedral particles within the grains appear to be a primary phase which forms prior to the $\alpha$-Mg phase given their position in the centre of the grains. There is a large volume fraction of fine lamellar phase and less, but still significant amount, of small blocky intermetallic phase as part of the eutectic distributed in the interdendritic regions.

XRD analysis was performed on a polished sample (Fig. 4). The XRD analysis reveals four main phases in the as-cast sample: $\alpha$-Mg, Al$_5$La$_2$, Mg$_2$La and (Al,Mg)$_3$La. In addition, there is a minimal amount of the (Al$_2$Si)$_3$La$_2$ phase with a hexagonal structure [38], which is isostructural with the Al$_5$La$_2$ phase. The lattice parameters between these two phases are slightly different. Some of the peaks of (Al$_2$Si)$_3$La$_2$ and Al$_5$La$_2$ overlap, which makes the lattice parameter determination for (Al$_2$Si)$_3$La$_2$ less reliable. Table 2 shows the refined lattice parameters of the identified phases in the as-cast sample. In this study, the lattice parameters of Al$_5$La$_2$ are different from those in the ICDD database. This is in agreement with a previous study [3], in which the lattice parameters of Al$_{2.12}$La$_{0.88}$ (Al$_5$La$_2$) are smaller than those in the ICDD database.

The phases identified in the XRD analysis have also been further characterised using TEM, as shown in Fig. 5. The selected area electron diffraction (SAED) and TEM-EDS have confirmed that the polyhedral microstructure belongs to an Al-La intermetallic phase with a nominal composition varying between an Al:La ratio of 2–2.5. Given this variability, it is perhaps more appropriate to call...
this phase $\text{Al}_2\text{La}_{1-x}$. The compositional stability of this phase (range of $x$ values) should be investigated further. However, XRD analysis shows that the crystal structure of this phase is hexagonal, which indicates that it is what has been previously identified as $\text{Al}_2\text{La}_3$ [3,39,40]. Hence, this phase is denoted as $\text{Al}_5\text{La}_2$ in this paper. In addition, there is an acicular phase that has also been identified as the $\text{Al}_5\text{La}_2$ phase. The lamellar intermetallic phase has been identified as the $\text{Mg}_{12}\text{La}$ eutectic phase. The TEM-EDS analysis indicates the composition of this phase is $\text{Mg}_{89.3}\text{Al}_{3.7}\text{La}_{7.0}$ (at.%), which is close to the nominal stoichiometry of the $\text{Mg}_{12}\text{La}$ phase. Lastly, the small blocky particles in the alloy were identified as the $(\text{Al, Mg})_3\text{La}$ phase [36]. Hence, the phases present in the alloy can be summarised as $\alpha\text{-Mg}$, polyhedral $\text{Al}_5\text{La}_2$, acicular $\text{Al}_5\text{La}_2$, $\text{Mg}_{12}\text{La}$ and $(\text{AlMg})_3\text{La}$. The TEM-EDS and SEM-EDS analysis reveal that there is a small amount of $(\text{AlSi})_5\text{La}_2$ in the ALa314 alloy which is in agreement with the XRD analysis; it has a larger polyhedral-shaped morphology than the $\text{Al}_5\text{La}_2$ phase. It is likely this phase has formed due to the small Si impurity in the alloy.

### 3.4. Thermodynamic predictions

The ALa314 alloy is located in the $\alpha\text{-Mg}$ region in the current phase diagram (Fig. 6a) [41,42]. The solidification sequence is predicted by the Scheil-Gulliver (non-equilibrium) equation and Lever (equilibrium) rule using the most recent magnesium database, PanMg 2018 [37] from Pandat®. The Scheil-Gulliver prediction (Fig. 6b) shows the formation of primary $\alpha\text{-Mg}$ (~600 °C), followed by the $\text{Mg}_{12}\text{La}$ phase (~595 °C) and lastly the cubic $\text{Al}_2\text{La}$ phase (~586 °C), sequentially. The equilibrium Lever simulation predicts the primary phase is again $\alpha\text{-Mg}$ (~600 °C), followed by $\text{Mg}_{12}\text{La}$ phase (~595 °C), and cubic $\text{Al}_2\text{La}$ phase (~586 °C). At much lower temperatures it predicts that the $\text{Al}_2\text{La}$ phase transforms into $\text{Al}_1\text{La}_{13}$ (~352 °C) and finally into $\text{Al}_1\text{La}_{13}$ (~198 °C) although these reactions are unlikely to be observed in a solidified microstructure. Interestingly both simulations do not predict a primary intermetallic phase which is clearly observed in the synchrotron study (Fig. 1).

### Table 2

<table>
<thead>
<tr>
<th>Phase</th>
<th>Space group</th>
<th>Refined Lattice Parameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha\text{-Mg}$</td>
<td>$P6_3/mmc$</td>
<td>$a = 0.320992 (7)$, $b = -$, $c = 0.52106 (1)$</td>
</tr>
<tr>
<td>$\text{Mg}_{12}\text{La}$</td>
<td>$I4/mmm$</td>
<td>$a = 1.02990 (3)$, $b = -$, $c = 0.59242 (2)$</td>
</tr>
<tr>
<td>$\text{Al}_5\text{La}_2$</td>
<td>$P6/mmm$</td>
<td>$a = 0.44781 (3)$, $b = -$, $c = 0.43119 (5)$</td>
</tr>
<tr>
<td>$(\text{AlMg})_3\text{La}$</td>
<td>$C222_1$</td>
<td>$a = 0.4349 (3)$, $b = 1.917 (1)$, $c = 0.4441 (3)$</td>
</tr>
<tr>
<td>$(\text{AlSi})_5\text{La}_2$</td>
<td>$P6/mmm$</td>
<td>$a = 0.4440 (5)$, $b = -$, $c = 0.4352 (9)$</td>
</tr>
</tbody>
</table>

### Fig. 5

Transition Electron Microscopy images, microbeam electron diffraction patterns and EDX spectra show the microstructure and identification of intermetallic phases in the as-cast ALa314. (a) The polyhedral intermetallic phase was identified to be primary $(\text{AlSi})_5\text{La}_2$, (b) the acicular-shaped intermetallic phase was identified to be eutectic $\text{Al}_5\text{La}_2$, (c) the lamellar-like intermetallic phase was identified to be $\text{Mg}_{12}\text{La}$ and (d) the blocky and particulate intermetallic phase was identified to be $(\text{AlMg})_3\text{La}$.

### Fig. 6

(a) Mg-rich phase diagram of the Mg-Al-La system with a black dashed arrowed line showing the predicted solidification path, and (b) solidification sequence predicted by Scheil-Gulliver equation using PanMg 2018 [37].
4. Discussion

The results have highlighted three key points that particularly require further discussion: (i) the solidification sequence of the alloy, (ii) the observed discrepancies from the current phase diagram [37] predictions, and (iii) the formation of Al5La2 as the primary intermetallic phase and its role in the nucleation of α-Mg.

4.1. Solidification sequence

During solidification in the in-situ synchrotron experiment, a La-containing intermetallic phase (primary Al5La2 phase) forms as the primary phase, as shown in Fig. 1 (Reaction 1). This reaction corresponds to the first peak in the cooling curves and their first derivative curves from thermal analysis (Fig. 2 – Reaction 1), in which the primary intermetallic phase appears to form at approximately 630 °C. The SEM and TEM analysis, as shown in Figs. 3 and 5, shows the La-containing primary intermetallic phase with a polyhedral morphology in the centre of the grains, indexed with a hexagonal (P6/mmm) structure with lattice parameters a = 0.44781 nm and c = 0.43119 nm. There is a discrepancy as to the temperature at which the first particles form. Interestingly, a very small amount of (Al,Si)5La2 was observed which may precipitate in minimal quantities at higher temperatures explaining the high temperature particles that were sparingly observed.

The second reaction in the solidification process is the nucleation and growth of α-Mg grains. The thermal analysis shows that the second reaction starts at approximately 617 °C. Microstructural observations show that the α-Mg grains have an equiaxed dendritic morphology (Fig. 3). The in-situ observations shown in Fig. 1 (Reaction 2), showed that some of the α-Mg nucleated directly on the primary Al5La2 phase. Ex-situ observations in Fig. 3 also showed Al5La2 particles located at the centre of α-Mg grains. Almost immediately after the nucleation of α-Mg, some Al5La2 particles appeared at the same time as the α-Mg phase, as shown in Fig. 1 (Reaction 2). This indicates that this reaction appears to be a eutectic containing α-Mg and Al5La2. The SEM and TEM micrographs, as shown in Figs. 3 and 5, also indicate that the eutectic Al5La2 phase has an acicular morphology.

The third reaction in the real-time solidification process is the formation of a binary eutectic α-Mg+Mg12La. The thermal analysis shows that it occurs at approximately 609 °C (Fig. 2), which is just under the binary eutectic temperature for Mg-La at about 612 °C [43–45]. The SEM and TEM analyses reveal that the binary eutectic Mg12La phase has a fine lamellar morphology, as shown in Figs. 3 and 5, respectively which fits with previous observations [43]. Within the binary eutectic α-Mg+Mg12La, (Al,Mg)3La is also observed (Figs. 3 and 5). This indicates that the final eutectic (Reaction 4) is likely to be a ternary eutectic producing α-Mg+Mg12La+(Al,Mg)3La at a temperature of approximately 602 °C. This suggests that the binary eutectic (Reaction 3) is a mono-variant eutectic due to the influence of the Al leading to the temperature being a little below the binary eutectic moving towards the final ternary eutectic. The (Al,Mg)3La particles were not observed in the synchrotron because they could not be resolved on the low magnification backline.

4.2. The comparison of experimental results and thermodynamic predictions

Table 3 summarises the solidification sequence from the thermodynamic predictions and the observations in this work. It is clear that there are discrepancies in both the sequence of reactions and the temperatures at which they occur.

Firstly, solidification begins (and ends) at much higher temperatures in the experimental alloy than in the predictions. It is apparent that the AlMg314 alloy is a hyper-eutectic alloy with the formation of primary intermetallic Al5La2 as the first phase. This is not predicted in the thermodynamic calculations indicating that the composition of the eutectic valley is not correct in the current predictions. This also affects the prediction of the co-formation of eutectic α-Mg+Al5La2 which is the next stage of the solidification sequence.

Another discrepancy in the early stages of solidification is that the thermodynamics predicts the formation of Al5La2 whilst Al5La2 was observed to form. Al5La2 is a phase known to the database and can be found by turning off the formation of Al5La2, which reveals Al5La2 as a metastable phase (Fig. 7). Interestingly, an extension of the metastable liquidus line for Al5La2 could predict it being the stable phase at compositions similar to the alloy studied. Hence Al5La2 may be stable or only slightly metastable in the alloy studied. Further consideration of the formation of this phase may also lead to a prediction of an increase in the eutectic temperature and reduction in the eutectic composition which could go a long way to explaining the observations in the current work.

The formation of the eutectic α-Mg+Mg12La is observed and predicted although the temperature at which this occurs is quite different from the predictions. The observations fit more closely with the temperature at which the binary Mg-La eutectic is known to occur (~612 °C) [43–45]. Interrogation of the liquidus surface of the Mg-Al-La phase diagram (Fig. 6a) shows that the binary Mg-La is correct in the predictions, but there is a steep mono-variant eutectic reaction valley down to the ternary L→α-Mg+Mg12La+Al5La reaction at 586 °C. The observed reaction, in contrast, involves the newly identified phase (AlMg)3La [36] as well as α-Mg+Mg12La at 602 °C. It appears that this reaction is currently unknown to the database hence incorporation of this phase will also improve the thermodynamic predictions.

4.3. Nucleant potency of primary Al5La2 particles

It appears from both the synchrotron study (Fig. 1) and microstructural analysis (Fig. 2) that α-Mg grains may form on Al5La2 particles that are sometimes found at the centre of grains. Whilst it is difficult to locate the active heterogeneous nucleation sites for α-Mg phase during solidification, analysis of the crystallographic matching between the α-Mg phase and the primary intermetallic phase, Al5La2, in the Mg3Al14La alloy can help to identify whether Al5La2 is a potent nucleant. The edge-to-edge matching (E2EM) model [46–48] was adopted to perform a theoretical misfit analysis.

The α-Mg phase has a simple hexagonal unit cell (a = 0.3209 nm and c = 0.5211 nm), and the most closed-packed (CP) rows run along <2TT>5-Mg direction. The superscript ‘S’ indicates this is a straight atomic row. The atomic configuration of Mg atoms in the most CP plane (0002) that carries <2TT>5-Mg CP rows is graphically illustrated in Fig. 8a. On the other hand, the Al5La2 phase has a hexagonal structure (a = 0.4478 nm and c = 0.4347 nm). The only straight CP row runs along the <0001>5-Al5La2 direction (Fig. 8b). By comparing the interatomic spacing along the CP row pair between <2TT>5-Mg and <0001>5-Al5La2, i.e. 0.321 nm and 0.435 nm, respectively, the resultant misfit value, f, is as large as 26.2%, which is far beyond the empirical threshold, 10%. This means the chance of forming an energetically favourable orientation relationship (OR) between the α-Mg phase and the Al5La2 phase is small.

Furthermore, approximately 15 α-Mg grains containing a polyhedral Al5La2 particle at their grain centre were examined, and no reproducible orientation relationship could be found based on EBSD mapping. This observation supports the conclusion made from the E2EM predictions. Although the crystallography of the
primary Al₅La₂ particles is not favourable for nucleating α-Mg grains, given the relatively large size of these polyhedral particles, the undercooling required for nucleation could be reduced according to the Free Growth model [49]. Hence, it is possible that some Al₅La₂ particles are more effective nucleation sites than impurities that may also be present. This explains why some of the α-Mg grains are observed to form around these particles and the grain size is not small given the number of particles present (Fig. 1).

5. Conclusions

Through a combination of synchrotron radiography, thermal analysis and microstructural characterisation, the solidification sequence of Mg-3Al-14La alloy has been determined and compared with thermodynamic predictions. The Mg-3Al-14La alloy is found to be a hyper-eutectic alloy, with the pro-eutectic Al₅La₂ phase precipitating first. This is followed by a mono-variant eutectic reaction with α-Mg + Al₅La₂ as the products, then a mono-variant eutectic with α-Mg + Mg₁₂La as the products before finishing with a ternary eutectic with α-Mg + Mg₁₂La + (Al,Mg)₃La as the products. There are a number of discrepancies between the experimental observations and the current thermodynamic predictions. In particular, the current thermodynamic description does not predict the formation of a hyper-eutectic phase, and that the first intermetallic to form is Al₅La₂ rather than the predicted Al₂La. Whilst

![Figure 7](image1.png)

Fig. 7. Sectional view with and without Al₂La suppressed and generated by Pandat using the PanMg 2018 database [37]. The green dashed line shows a hypothetical extension of the Al₅La₂ liquidus line which could demonstrate a region where Al₅La₂ may be stable. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

![Figure 8](image2.png)

Fig. 8. The atomic configuration in the CP plane of (a) (0002)Mg and (b) (12̅10)Al₅La₂. The most CP rows are highlighted by bold solid lines.

<table>
<thead>
<tr>
<th>Source</th>
<th>Temperature (°C)</th>
<th>Phase transformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermodynamic predictions [PanMg 2018 [37]]</td>
<td>599.8</td>
<td>Liquid → α-Mg</td>
</tr>
<tr>
<td></td>
<td>594.7</td>
<td>Liquid → α-Mg + Mg₁₂La</td>
</tr>
<tr>
<td></td>
<td>586.0</td>
<td>Liquid → α-Mg + Mg₁₂La + Al₂La</td>
</tr>
<tr>
<td>This work</td>
<td>630.0</td>
<td>Liquid → Primary Al₅La₂</td>
</tr>
<tr>
<td></td>
<td>617.0</td>
<td>Liquid → α-Mg + Al₅La₂</td>
</tr>
<tr>
<td></td>
<td>609.0</td>
<td>Liquid → α-Mg + Mg₁₂La</td>
</tr>
<tr>
<td></td>
<td>602.0</td>
<td>Liquid → α-Mg + Mg₁₂La + (Al,Mg)₃La</td>
</tr>
</tbody>
</table>

**Table 3** Solidification sequence of Al₅La₂ simulated by Pandat [37] and thermal analysis data.
some α-Mg grains appear to nucleate on Al5La2 particles, the Al5La2 phase is probably not a potent nucleant for α-Mg grains because no favourable orientation relationship between α-Mg and the Al5La2 phase can be predicted or observed. Finally, the newly identified (Al,Mg)La phase is observed in the last solidified ternary eutectic.

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Chapter 7
Revisiting the intermetallic phases in high-pressure die-cast Mg–4Al–4Ce and Mg–4Al–4La alloys

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Suming Zhu a,b, Charlotte Wong a, Mark J. Styles c, Trevor B. Abbott a,b,d, Jian-Feng Nie b, Mark A. Easton a

a School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
b Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
c CSIRO Manufacturing, Clayton, Victoria 3168, Australia
d Magontec Limited, Sydney, New South Wales 2000, Australia

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Revisiting the intermetallic phases in high-pressure die-cast Mg–4Al–4Ce and Mg–4Al–4La alloys

Suming Zhua,b,⁎, Charlotte Wonga, Mark J. Stylesc, Trevor B. Abbottb,b,d, Jian-Feng Nieb, Mark A. Eastona

a School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
b Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
c CSIRO Manufacturing, Clayton, Victoria 3168, Australia
d Magontec Limited, Sydney, New South Wales 2000, Australia

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ABSTRACT

Mg–Al–RE based alloys such as AE42 (Mg–4Al–2RE) and AE44 (Mg–4Al–4RE) are commonly known to contain A111RE3 and Al2RE intermetallic phases, with the former being predominant. However, it was found recently that the predominant intermetallic phase in a gravity-cast Mg–4.5Al–6.3La alloy is not A111La3 but a new ternary phase with the composition of (Al,Mg)3La. In this work, the intermetallic phases in high-pressure die-cast Mg–4Al–4Ce and Mg–4Al–4La alloys are thus re-examined by X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It is shown that the predominant intermetallic phase is A111Ce3 in the die-cast Mg–4Al–4Ce alloy but (Al,Mg)3La in the die-cast Mg–4Al–4La alloy. Both A111Ce3 and (Al,Mg)3La remain thermally stable upon annealing at 500 °C for 100 h and are most likely equilibrium phases in each alloy. This study provides strong evidence that the formation of intermetallic phases in Mg–Al–RE alloys is affected by the choice of individual RE elements.

1. Introduction

Mg–Al–rare earth (RE) based alloys are one family of magnesium die-casting alloys developed for elevated temperature applications. Two notable alloys are AE42 (Mg–4Al–2RE–0.3Mn, wt%) [1] and AE44 (Mg–4Al–4RE–0.3Mn) [2]. These alloys exhibit superior creep resistance to Mg–Al based alloys such as AZ91 (Mg–9Al–1Zn) and AM60 (Mg–6Al–0.3Mn), owing to the formation of more stable Al–RE intermetallic phases instead of Mg17Al12 phase [3] and the beneficial effect of the minor Mn additions in these alloys [4].

The intermetallic phases and their thermal stability in die-cast Mg–Al–RE alloys have been investigated previously by a number of studies [5–11]. There is a general agreement that A111RE3 (body-centred orthorhombic structure) is the predominant intermetallic phase in these alloys, with Al2RE (diamond structure) being the minor one. Occasionally, Al10RE2Mn7 (hexagonal structure) can also be detected, which is associated with the addition of 0.15–0.5 wt% Mn for improvement of corrosion resistance. However, there seems to be a debate regarding the thermal stability of A111RE3 phase. Some studies [6,9,10] reported that A111RE3 is unstable and decomposes to Al2RE at elevated temperatures, releasing Al that subsequently reacts with Mg to form Mg12Al12. In contrast, other studies [5,7,8,11] reported that A111RE3 is thermally stable at least up to 200 °C. To resolve this dispute, first-principles density functional calculations were conducted recently on the thermal stability of A111RE3 phase [12,13]. According to these studies, A111RE3 should be thermodynamically stable and will not decompose to Al2RE at temperatures up to 450 °C for La, Ce, Pr, Nd and Sm, but it may become unstable for Yb, Dy, Y, Ho and Er.

Traditionally, RE elements were added to Mg–Al–RE alloys in the form of misch metal, with Ce being the most abundant element, followed by La, Nd and Pr. However, the increased demand for Nd in magnetic applications over the past decades has led to two-element misch metal (containing only Ce and La) becoming considerably cheaper as the by-products of the separation of Nd and Pr from the four-element misch metal. As such, efforts have been made to develop cost-effective die-cast Mg–Al–RE alloys that contain either La [14–16] or Ce [16,17] or La + Ce misch metal [9,10]. From these studies, the choice of RE elements appears to have a discernible influence on the mechanical properties, especially creep resistance, of die-cast Mg–Al–RE alloys. While earlier studies [9,14,17] related the influence of RE to the thermal stability of the A111RE3 phase, later work [16] suggested that the fraction of intermetallic phases and the content of Mn are more

⁎ Corresponding author at: School of Engineering, RMIT University, Carlton, Victoria 3053, Australia.
E-mail address: suming.zhu@rmit.edu.au (S. Zhu).

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likely to be influential. It should be pointed out that, in all studies, $A_{11}\text{RE}_3$ was identified to be the predominant intermetallic phase, regardless the choice of RE elements.

A new ternary phase with the composition of $(\text{AlMg}_2)\text{La}$ was recently identified in a gravity-cast Mg-$4.5\text{Al}-6.3\text{La}$ alloy [18]. This phase was found to have an orthorhombic structure with a space group of $C222_1$ and lattice parameters of $a = 4.3365$ Å, $b = 18.8674$ Å and $c = 4.4242$ Å, which is distinctly different from that of the binary $A_{11}\text{La}_3$ or $A_{12}\text{La}_2$. In the present work, the intermetallic phases in the die-cast Mg-$4\text{Al}-4\text{La}$ alloy [16] are thus revisited. For comparison, the die-cast Mg-$4\text{Al}-4\text{Ce}$ alloy [16] is also re-examined. The purposes of this study are (i) to determine whether the $(\text{AlMg}_2)\text{La}$ phase is present in die-cast Mg-$A_{11}\text{La}$ alloys or not and (ii) to clarify if the formation of intermetallic phases in Mg-$A_{11}\text{RE}$ alloys is affected by individual RE elements. The information obtained should be helpful for understanding the mechanical properties of die-cast Mg-$A_{11}\text{RE}$ alloys and for designing new Mg-$A_{11}\text{RE}$ alloys.

2. Experimental methods

The Mg-$4\text{Al}-4\text{Ce}$ (ACe44) and Mg-$4\text{Al}-4\text{Ce}$ (ALa44) alloys used in this work were produced by high-pressure die-casting. The details of alloy preparation can be found elsewhere [19] but are briefly summarized here. The alloys were cast in a 250 t Toshiba cold chamber high-pressure die-casting machine. The alloy melts were produced in a resistance heated crucible and held at around 700 °C before casting. During melting and holding, the melts were protected using AM-cover (HFC-134a in CO$_2$ carrier gas). The temperature of the oil for heating up makes it distinguishable from the $A_{11}\text{Ce}_3$ phase although the difference in thermal stability for the ternary $A_{12}\text{CeSi}_2\text{-x}$ phase is only in this study.

Table 1

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Al%</th>
<th>Mn%</th>
<th>Ce%</th>
<th>La%</th>
<th>Nd%</th>
<th>Zn%</th>
<th>Fe ppm</th>
<th>Si ppm</th>
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</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>3.97</td>
<td>0.14</td>
<td>4.04</td>
<td>0.03</td>
<td>&lt; 0.005</td>
<td>0.008</td>
<td>114</td>
<td>410</td>
</tr>
<tr>
<td>ALa44</td>
<td>4.05</td>
<td>0.27</td>
<td>0.01</td>
<td>3.87</td>
<td>&lt; 0.005</td>
<td>0.04</td>
<td>70</td>
<td>80</td>
</tr>
</tbody>
</table>

The phases identified by XRD for the as-cast ACe44 and ALa44 alloys are shown in Fig. 1. From the S values, the fitting of the calculated pattern to the measured pattern appears to be sufficiently good for both alloys. Estimates for the phase fractions (calculated using the Hill-Hoard method [23]) are included for the purposes of this study. The ternary $A_{12}\text{CeSi}_2\text{-x}$ phase is consistent with those reported previously [16,17]. The Al$_{11}$Ce$_3$ phase was identified in the previous studies. For ACe44, the XRD analysis reveals the following four intermetallic phases: $A_{11}\text{Ce}_3$, $A_{12}\text{Ce}_2$, Al$_5$Ce and Al$_{12}\text{CeSi}_2\text{-x}$ with $A_{11}\text{Ce}_3$ being the predominant phase. For ALa44, phase is identified on the assumption that it is isostuctural to Al$_{12}\text{La}_2$ [21] or Al$_{12}\text{La}_3$ [24], which has a hexagonal crystal structure.

2.1. Alloy composition

The chemical compositions of the alloys were analysed by inductively coupled plasma-optical emission spectroscopy (ICP-OES) and the results are shown in Table 1. It can be seen that the analysed contents of Al and Ce or La are quite close to the nominal ones. Both alloys also contain minor Mn, which is commonly added to control Fe content for improved corrosion resistance. It is noted that the level of impurity Si is relatively high (410 ppm) in ACe44, which will be shown to affect the formation of intermetallic phases.

3. Results

3.1. Alloy composition

The as-cast alloys were further annealed at 500 °C for 100 h to investigate the thermal stability of intermetallic phases and to reveal
which are metastable phases and which are equilibrium phases in each alloy. The XRD results of the annealed ACe44 and ALa44 are shown in Fig. 5. For ALa44, the following intermetallic phases are identified after the annealing: \((\text{Al,Mg})_3\text{La}, \text{Al}_{11}\text{La}_3\) and \(\text{Al}_8\text{Mn}_4\text{La}\), with the \((\text{Al,Mg})_3\text{La}\) phase still being predominant. The common Mn-containing intermetallic phase in die-cast Mg–Al–RE alloys has been widely reported [5,7,8,11] to be \(\text{Al}_{10}\text{Mn}_7\text{RE}_2\) although a recent work [26] reported the co-existence of \(\text{Al}_{10}\text{Mn}_7\text{RE}_2\) with \(\text{Al}_{8}\text{Mn}_4\text{RE}\) in a die-cast AE44 alloy. Given that \(\text{Al}_8\text{Mn}_4\text{La}\) is identified in ALa44 after annealing at 500 °C, it is speculated that this phase probably transforms from \(\text{Al}_{10}\text{Mn}_7\text{La}_2\) in the as-cast ALa44. However, no \(\text{Al}_{10}\text{Mn}_7\text{La}_2\) phase was able to be detected by XRD (Fig. 1a), possibly because of its low fraction and pattern overlapping with other phases. As \(\text{Al}_8\text{Mn}_4\text{La}\) is a minor phase and not the focus of this paper, it will not be addressed further. Since \(\text{Al}_8\text{Mn}_4\text{La}\) is still predominant after annealing, it is thus most likely an equilibrium phase in ALa44. In contrast, the disappearance of the \(\text{Al}_{11}\text{La}_2\) phase after annealing suggests that \(\text{Al}_{11}\text{La}_2\) is most likely a metastable phase in ALa44. The case for ACe44 is more complicated since five intermetallic phases are identified after annealing, i.e. \(\text{Al}_{11}\text{Ce}_3\), \(\text{Al}_5\text{Ce}\), \(\text{Al}_{11}\text{Ce}_6\), \(\text{Al}_{11}\text{CeSi}_2\), and \(\text{Al}_8\text{Mn}_4\text{Ce}\). Like the \(\text{Al}_8\text{Mn}_4\text{La}\) phase in ALa44, the \(\text{Al}_8\text{Mn}_4\text{Ce}\) phase will be neglected here. The remaining of \(\text{Al}_{11}\text{CeSi}_2\) after annealing suggests that this ternary phase is stable at 500 °C, which is consistent with the \(\text{Al}–\text{Ce}–\text{Si}\) phase equilibria [27]. The formation of \(\text{Al}_5\text{Ce}\) phase is unexpected and is thus further analysed by TEM. In view of the fact that \(\text{Al}_{11}\text{Ce}_3\) is still the most abundant phase after annealing, it is reasonable to deduce that it is most likely an equilibrium phase in ACe44. Since the \(\text{Al}_5\text{Ce}_2\) phase is not observed after annealing, it is most likely a metastable phase in ACe44, just like the \(\text{Al}_{11}\text{La}_2\) phase in ALa44. The SEM micrographs of the annealed ACe44 and ALa44 alloys are shown in Fig. 6. It is apparent that the predominant intermetallic phases in both alloys have undergone significant spheroidization in morphology after annealing even though they retain the same identity as in the as-cast state. Similar morphological changes of intermetallic phases have been reported in die-cast Mg–Al–RE alloys after ageing or creep testing at temperatures in the range 150–200 °C, and was previously used as evidence for decomposition of the \(\text{Al}_{11}\text{RE}_3\) phase into the \(\text{Al}_2\text{RE}\) phase [6,9,10]. However, this decomposition mechanism is not supported by the current study.

The TEM analysis of the \(\text{Al}_3\text{Ce}\) phase in the annealed ACe44 is shown in Fig. 7. The \(\text{Al}_3\text{Ce}\) phase appears to be coarse and blocky particles in the microstructure. It should be pointed out that no \(\text{Al}_3\text{Ce}\) phase has been previously observed in any Mg–4Al–4Ce alloy. More work is needed to understand if this \(\text{Al}_3\text{Ce}\) is an equilibrium phase and how it is formed.

4. Discussion

The intermetallic phases identified in ACe44 and ALa44 by the Rietveld analysis of the XRD data are summarized Table 2. Estimates for the phase fractions and lattice parameters are included for comparison. While the absolute values are influenced by factors such as the α-Mg
grain size (particle statistics), these estimates allow the major and minor intermetallic phases to be identified. As shown in the preceding section, most intermetallic phases identified by XRD have been confirmed by the SEM and TEM analyses. Two important findings are noted in the phase identification, one is the presence of the Al$_5$RE$_2$ phase in both alloys in the as-cast state and the other is the presence of

![TEM bright field images, selected area electron diffraction patterns and EDS spectra of the typical intermetallic phases in the as-cast ACe44 alloy: (a) Al$_{11}$Ce$_3$, (b) Al$_2$Ce, (c) Al$_5$Ce$_2$ and (d) Al$_x$CeSi$_{2-x}$.](image)
the (Al,Mg)\textsubscript{3}La phase in ALa\textsubscript{44}, which are discussed as follows.

### 4.1. The Al\textsubscript{5}RE\textsubscript{2} phase in the as-cast ACe\textsubscript{44} and ALa\textsubscript{44}

It is interesting to note that the Al\textsubscript{5}RE\textsubscript{2} phase is present in both alloys in the die-cast state, especially Al\textsubscript{5}Ce\textsubscript{2} in ACe\textsubscript{44}. Formation of Al\textsubscript{5}RE\textsubscript{2} was also observed in sand-cast Mg–3Al–10Ce [28], Mg–4Al–12Ce [28] and Mg–3Al–14 La [29] alloys. Unlike the Al\textsubscript{5}La\textsubscript{2} phase, which exists in the binary Al–La phase diagram [30], there is no Al\textsubscript{5}Ce\textsubscript{2} phase included in the binary Al–Ce system [30]. However, Gao et al. [31] raised a question about the possible presence of the Al\textsubscript{5}Ce\textsubscript{2} phase in the Al–Ce system when studying the lattice stability of Al–RE binary systems using a first-principles approach. Thus, the current Al–Ce phase diagram may need to be re-examined.

A similar phase, Al\textsubscript{2.12}RE\textsubscript{0.88}, was identified by Rzychoń et al. [8] in die-cast AE\textsubscript{44}. According to Rzychoń et al. [8], Al\textsubscript{2.12}RE\textsubscript{0.88} forms as a result of high solidification rate during high-pressure die-casting, which explains why they did not observe this phase in slowly cooled AE\textsubscript{44} prepared by sand-casting [32]. Therefore, it is not surprising to see Al\textsubscript{5}RE\textsubscript{2} phase in the die-cast ACe\textsubscript{44} and ALa\textsubscript{44} alloys. Rzychoń et al. [8] also reported that Al\textsubscript{2.12}RE\textsubscript{0.88} is a metastable phase and transforms to Al\textsubscript{5}RE after ageing at 175 °C for long times (1000 h and 3000 h). This claim seems to be supported by the current study since no Al\textsubscript{5}RE\textsubscript{2} phase remains after annealing at 500 °C for 100 h. However, it is unclear why Al\textsubscript{5}RE\textsubscript{2} is formed instead of Al\textsubscript{5}RE at high solidification rates in these alloys. Also, it remains to be explained why Al\textsubscript{5}RE\textsubscript{2} phase was also formed in the sand-cast Mg–3Al–10Ce [28], Mg–4Al–12Ce [28] and Mg–3Al–14 La [29], where the solidification rate was not very high.

### 4.2. The (Al,Mg)\textsubscript{3}La phase in ALa\textsubscript{44}

The most striking finding of this study is that the predominant intermetallic phase in ALa\textsubscript{44} is (Al,Mg)\textsubscript{3}La, rather than Al\textsubscript{11}La\textsubscript{3} as commonly accepted. The Al\textsubscript{11}La\textsubscript{3} phase is indeed observed in the as-cast state, but only as a minor one. Moreover, the (Al,Mg)\textsubscript{3}La phase remains stable at 500 °C and thus is most likely an equilibrium phase in
This is in contrast to the case of ACe44 in which A11Ce3 is the predominant intermetallic phase and is stable at 500 °C. Hence, it can be concluded that the choice of individual RE elements has a great influence on the formation of intermetallic phases in Mg–Al–RE alloys.

The observation of (Al,Mg)3La phase in ALa44 validates the recent work on gravity-cast Mg–4.5Al–6.3La alloy [18], in which (Al,Mg)3La was found and identified for the first time. The fact that no A111La3 was detected in the relatively slowly solidified Mg–4.5Al–6.3La alloy...
implies that Al\textsubscript{11}La\textsubscript{3} is probably a metastable phase and is only formed at high solidification rates in Mg–Al–La alloys, just like the Al\textsubscript{11}La\textsubscript{2} phase. Similarly, further work is needed to understand why the Al\textsubscript{11}La\textsubscript{3} phase is formed during die-casting in ALa\textsubscript{44}.

5. Conclusions

The intermetallic phases in high-pressure die-cast Mg–4Al–4Ce and Mg–4Al–4La alloys have been re-examined and the following conclusions can be drawn:

1. Al\textsubscript{11}Ce\textsubscript{3} is the predominant intermetallic phase in the die-cast Mg–4Al–4Ce alloy, with Al\textsubscript{12}Ce\textsubscript{2} and Al\textsubscript{12}Ce\textsubscript{3} being the minor ones. Al\textsubscript{12}Ce\textsubscript{3} is also present due to the relatively high Si level.
2. (Al,Mg)\textsubscript{2}La is the predominant intermetallic phase in the die-cast Mg–4Al–4La alloy, with Al\textsubscript{12}La\textsubscript{2} and Al\textsubscript{12}La\textsubscript{3} being the minor ones.
3. Al\textsubscript{17}Ce\textsubscript{2} and (Al,Mg)\textsubscript{2}La remain thermally stable upon annealing at 500 °C for 100 h and are most likely the equilibrium phase in each alloy.
4. The choice of individual RE elements has a great influence on the formation of intermetallic phases in Mg–Al–RE alloys.

Data availability statement

The raw/processed data required to reproduce these findings cannot be shared at this time due to technical or time limitations.

Acknowledgements

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References


Chapter 8

A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Charlotte Wong¹, Suming Zhu¹,⁴, Mark J. Styles², Trevor B. Abbott¹,⁴,⁵, Kazuhiro Nogita³, Jian-Feng Nie⁴, Mark A. Gibson¹,²,⁴, Mark A. Easton¹

¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia

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A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Title

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¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia

*Corresponding author: Mark Easton (mark.easton@rmit.edu.au)

Abstract

The microstructure of a series of sand-cast Mg-(3-4)Al-xCe and Mg-(3-4)Al-xLa alloys, where “x” ranges between 4 wt.% and 13 wt.%, has been characterised by scanning electron microscopy, X-ray powder diffraction and transmission electron microscopy. The experimentally identified phases have been compared with those from the Scheil-Gulliver and Lever predictions made using PANDAT®. As commonly reported in commercial Mg-Al-RE alloys (RE being Ce-rich mischmetal), Al₁₁Ce₃ was found to be the predominant intermetallic phase in the Mg-Al-xCe alloy series, particularly in ACe44. Al₂Ce and Al₃Ce₂ were also observed, and alloys with greater than 10 wt.% Ce, such as the ACe310 and ACe413 alloys, were found to be hyper-eutectic alloys with Al₂Ce as the primary phase. In the Mg-4Al-xLa alloys, the recently reported (Al,Mg)₃La phase was observed extensively and there was no evidence of either Al₁₁La₃ nor Al₂La phase. In addition, differences are noted between the current observations and the most recently published Mg-Al-Ce and Mg-Al-La phase diagrams.

Keywords: Mg–Al–La alloy; Mg–Al–Ce alloy; Microstructure characterization; Intermetallic phase; Gravity-cast; Sand-cast
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Introduction

Magnesium alloys are the lowest density structural metal alloys. This has motivated the development of lightweight components for automobiles due to the increasing demand for vehicle weight reduction to achieve high fuel efficiency [1, 2]. In addition, the excellent castability and low melting temperature of magnesium make it suitable for producing thin-walled and complex castings at a relatively low cost [3, 4]. The most commonly used magnesium alloys in current automotive applications are AZ91 (Mg-9Al-1Zn, all compositions are in weight percent unless otherwise specified), AM50 (Mg-5Al-0.4Mn) and AM60 (Mg-6Al-0.4Mn) [5]. However, these alloys have poor creep resistance at operating temperatures above 130°C, which makes them unsuitable for high-temperature powertrain applications [3]. This limitation has led to the development of new creep-resistant magnesium alloys based on the Mg-Al-RE (RE = Ce, La) systems for use in powertrain components, such as engine blocks and transmission cases, which are most commonly produced in cast aluminium alloys and cast iron [6].

AE44 (Mg-4Al-4RE, with “A” representing Al and “E” representing mischmetal) is a magnesium alloy that is increasingly used in higher performance applications. Currently, mischmetal is used in commercial AE44 alloys. Prior to 2011 a four-element mischmetal, which contains neodymium (Nd) and praseodymium (Pr) as well as cerium (Ce) and lanthanum (La) has been used [2]. Since Nd and Pr are in demand for magnetic applications, two element mischmetal containing only La and Ce is cheaper and has replaced four element mischmetal in the alloy [7]. However, some researchers have reported that different rare earths lead to different microstructures [7, 8] and may affect the performance of the alloys [7-10]. Consequently, understanding the role of different rare earth elements and their concentration on the performance and microstructure of these alloys is important both commercially and scientifically.

There have been several experimental investigations into the microstructure of AE alloys [8, 9, 11, 12]. The needle-like Al_{11}RE_{3} phase has been reported to be the dominant intermetallic phase [10, 13-17], and the particulate Al_{3}RE has been reported to be an additional minor phase [10, 13, 15, 16] in AE44 alloys. Previous studies have also been performed to understand the effect of RE on microstructure, including the refinement and morphology of α-Mg and intermetallic phases in AE alloys [7, 9, 18-21], but there are differences in the phases reported. For example, some studies [22, 23] reported that the microstructure of high pressure die-cast
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys (HPDC) AE44 alloys contain α-Mg, Al$_{11}$RE$_3$, Al$_2$RE, and Al$_3$RE$_2$ phases, however, other studies did not observe the Al$_3$RE$_2$ phase in the same alloy [19, 21, 24]. A previous study also observed Al$_{11}$RE$_3$ and Al$_{10}$RE$_3$Mn$_7$ in an HPDC AE41 alloy [14]. In addition, there have been studies on sand-cast AE44 and AE55 alloys, in which the microstructure was observed to contain α-Mg, Al$_{11}$RE$_3$, Al$_2$RE, and Al$_{10}$RE$_2$Mn$_7$ [23, 25, 26].

In ternary Mg-Al-Ce alloys, multiple studies [7, 9, 21] have reported similar phases to AE44 alloys. For example, HPDC ACe44 alloys have been reported to contain Al$_{11}$Ce$_3$ and Al$_2$Ce [7, 9, 21]. On the other hand, the literature on Mg-Al-La alloys with La as the individual RE alloying element has greater inconsistencies. For example, Zhang et al. [8, 9, 21] and Bai et al. [20] reported that the microstructure of HPDC and gravity cast ALa44 alloy consists of α-Mg and Al$_{11}$La$_3$ [9, 21]. Recently, Zhu et al. [7, 19, 24] identified the phases in ALa44 using X-ray powder diffraction (XRD) and selected area electron diffraction (SAED) patterns and found Al$_2$La in addition to the other phases. Zhang et al. [8] also proposed that the Al$_2$La phase would be present if the La content in the alloy is above 5.5 wt.%. This is in contradiction to Zhu et al. [19, 24] who observed Al$_2$La in a 4 wt.% La containing AE alloy. Another study claimed that an Mg-4Al-1.5La alloy contains α-Mg, Al$_{11}$La$_3$ and Al$_4$La using XRD [18]. Given that the RE/Al ratio is less than 0.5 in this alloy, Mg$_{17}$Al$_{12}$ would be expected [25, 27], but it was not observed in their alloy.

It is also apparent that the morphology of the intermetallics in Mg-Al-Ce and Mg-Al-La alloys are different, as reported in [28] (Chapter 7). However, despite the difference in microstructure and morphology in these alloys, it has been assumed that similar intermetallic phases are developed in these systems [7, 21]. The differences in the phases identified by different researchers in the AE alloys have instigated this investigation into the intermetallic phases present in these alloys.

**Experimental methods**

In this study, a series of sand-cast Mg-(3-4)Al-xCe and Mg-(3-4)Al-xLa alloys, where “x” ranges between 4 wt.% and 13 wt.%, were investigated. These alloys were prepared from pure elemental magnesium (99.95 %), aluminium (99.90 %), cerium (99.50 %) and lanthanum (99.90 %), respectively. Magnesium was melted first, then aluminium was added and finally the rare earths. The weighed elements were melted in a crucible under a cover gas of nitrogen and R134a. The molten alloy was stirred well after each addition, to ensure complete mixing. After the ingots were completely melted in the crucible, the alloy was gravity cast into a
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys
preheated sand mould. The mould was preheated to approximately 120 °C and the molten alloy
was poured into the mould when the mould temperature was approximately 95 °C. Increasing
the RE content in these alloys causes the liquidus temperature to increase. Hence, the pouring
temperature of the molten metal into the mould was between 720 °C and 800 °C depending on
the composition of the alloy. The chemical compositions of the alloys were determined by
inductively coupled plasma atomic emission spectroscopy (ICP-OES), as shown in Table 1.

<table>
<thead>
<tr>
<th>Nominal alloy</th>
<th>Ce</th>
<th>La</th>
<th>Al</th>
<th>Mn</th>
<th>Si</th>
<th>Mg</th>
</tr>
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<tr>
<td>ACe413</td>
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<td>0.021</td>
<td>0.019</td>
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<tr>
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<td>3.96</td>
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<td>0.022</td>
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</tr>
<tr>
<td>ALa413</td>
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<td>3.86</td>
<td>0.022</td>
<td>0.023</td>
<td>Bal.</td>
</tr>
</tbody>
</table>

Samples were taken from near the top of the mould where the pre-solidification cooling rate
was measured to be approximately 8 °C/s using a K-type thermocouple. For microstructural
examination, samples were ground, then diamond polished and finished with alumina
suspension to approximately 0.04 µm particle size. The samples were ultrasonically cleaned
for 180 seconds after each step of grinding and polishing.

Bulk identification of the phases in the as-cast alloys was undertaken by XRD using a Rigaku
Smartlab diffractometer fitted with a rotating CuKα anode, operated at 45 kV and 200 mA.
Diffraction patterns were obtained in the 2θ range of 15°-120° with an equivalent scan rate of
2 °/min and step size of 0.02°. Because the α-Mg grain size in the sand-cast samples is relatively
large the samples were continuously oscillated during the measurement and a 2D area detector
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys was used to capture as much of the Debye-Scherrer rings as possible, in order to maximise the particle statistics. While this approach provided accurate relative peak intensities for all of the intermetallic phases observed, the peak intensities of α-Mg were not suitable for quantitative analysis. Hence, during the XRD data analysis the α-Mg phase was modelled using the Pawley method [29], whereas the remaining intermetallic phases were modelled using the Rietveld method [30], as implemented in the Topas software package (version 5, Bruker). The structure models for the α-Mg, Al$_{11}$Ce$_3$, Al$_2$Ce, Mg$_{12}$Ce/La, (Al, Si)$_3$Ce/La$_2$, Al$_5$La$_2$, CeSi$_2$ and MgLa phases present in the alloys were taken from the Pearson handbook [31] and ICDD PDF-4+ database [32], whereas the structure for (Al, Mg)$_3$La and Al$_5$Ce$_2$ were taken from Wong et al. [33] and [34], respectively.

The as-cast microstructures were analysed using an FEI Quanta 200 scanning electron microscope (SEM) equipped with an Oxford Instruments X-MaxN 20 energy dispersive X-ray (EDX) spectrometer at 25 kV. The intermetallic phases in the alloys were further confirmed by transmission electron microscopy (TEM) in a JEOL 2100F TEM equipped with an Oxford X-MaxN 80T EDX spectrometer. The TEM foils were prepared by low-angle ion milling using a Gatan Precision Ion Polishing System (PIPS) at 4 keV with an incident angle of 4°.

The phases identified by XRD and TEM were compared with those predicted by the Scheil-Gulliver (non-equilibrium) and Lever (equilibrium) equations using PANDAT®, PanMagnesium 2018 database [35].

**Results**

**Microstructure overview**

The as-cast microstructure in the selected series of AE alloys was examined by SEM, as shown in Figure 1. The α-Mg dendrites are surrounded by the intermetallic phase(s) in the interdendritic and grain boundary regions. As the RE concentration increases from 4 wt.% to 7 wt.% Ce and 11 wt.% La, there are additional polyhedral intermetallic particles observed inside the grains. In addition, the amount of fine eutectic increases as the RE content increases; this is especially significant in Mg-Al-La alloys, as shown in Figure 1(g) and (h).
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Figure 1 Secondary electron micrographs of the sand-cast (a) ACE44, (b) ACE47, (c) ACE310, (d) ACE413, (e) ALa44, (f) ALa37, (g) ALa311 and (h) ALa413.
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

The morphology of the intermetallic phases in the Mg-Al-Ce and Mg-Al-La alloys is very different. For example, a long needle-like intermetallic phase is observed in the Mg-Al-La alloys but not in the Mg-Al-Ce alloys. In addition, the eutectic volume fraction in the Mg-Al-La alloys is greater than in the Mg-Al-Ce alloys. On the other hand, the fraction of the polyhedral intermetallic particles within the grains is much higher in the Mg-Al-Ce alloys compared to the Mg-Al-La alloys; this is especially clear in Figure 1(c).

**Phase identification in Mg-Al-Ce alloys**

The XRD patterns for the Mg-Al-Ce alloys are shown in Figure 2. The XRD analysis reveals that the ACe44 and ACe47 alloys contain α-Mg, Al₅Ce₂, Al₂Ce, Al₁₁Ce₃ and a small amount of both (Al,Si)₅Ce₂ and CeSi₂, as shown in Figure 2(a) and (b), respectively. When the Ce concentration reaches 10 wt.% in ACe310 and 13 wt.% in ACe413, as shown in Figure 2(c) and (d), the phases observed changes somewhat. The phases formed in these alloys are α-Mg, Al₅Ce₂, Al₂Ce, Mg₁₂Ce and again a small amount of (Al,Si)₅Ce₂ and CeSi₂. In these two alloys, Mg₁₂Ce is formed instead of the Al₁₁Ce₃ phase, which commonly appears in low Ce content alloys. In the present study, there are a few minor peaks that have not been identified. These low-intensity peaks may be attributed to oxide in the samples. There is also a small amount of Mg₁₇Al₁₂ observed in ACe44, as shown in Figure 3, but not in higher Ce-containing alloys. This phase is not identified using XRD due to the small volume fraction of this phase.
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Figure 2 XRD analysis of (a) ACe44, (b) ACe47, (c) ACe310 and (d) ACe413 alloys. The calculated patterns are represented in red and the experimental patterns in blue. The difference between the experimental and calculated patterns is represented in grey.
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

TEM images for the intermetallic phases in ACe44 alloys are shown in Figure 4. From the indexing of electron diffraction patterns, the intermetallic phases were confirmed to be Al$_{11}$Ce$_3$, Al$_2$Ce, Al$_3$Ce$_2$ and (Al,Si)$_3$Ce$_2$. SAED in combination with EDX confirms that the eutectic needle-like intermetallic phase is Al$_{11}$Ce$_3$; the particulate-shape intermetallic phase is Al$_2$Ce; the acicular phase is Al$_3$Ce$_2$/[(Al,Si)$_3$]Ce$_2$; and the eutectic lamellar-like phase is Mg$_{12}$Ce.
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Phase identification in Mg-Al-La alloys

The XRD patterns for the Mg-Al-La alloys are shown in Figure 5. The XRD analysis reveals that the ALa44 alloy contains α-Mg, Al5La2 and (Al,Mg)3La (Figure 5(a)). As the La content increases from 4 wt.% to 7 wt.% in ALa37, as shown in Figure 5(b), (Al,Si)5La2 and Mg12La are also observed in addition to the phases found in ALa44 alloy. These phases are the same in ALa311, as shown in Figure 5(c). The (Al,Si)5La2 phase is present due to the presence of trace...
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys amounts of Si in this alloy. However, there is no $(\text{Al,Si})_5\text{La}_2$ observed in ALa413, and instead there is a small amount of the cubic MgLa phase, as shown in Figure 5(d).

![Figure 5](image.png)

*Figure 5 XRD analysis of (a) ALa44, (b) ALa37, (c) ALa311 and (d) ALa413 alloys. The calculated patterns are represented in red and the experimental patterns in blue. The difference between the experimental and calculated patterns is represented in grey.*

Similar to the ACe44, there is a small amount of Mg$_{17}$Al$_{12}$ observed in the ALa44, as shown in Figure 6. Mg$_{17}$Al$_{12}$ was not observed in higher La-containing alloys. The intermetallic phases identified in the Mg-Al-La alloys have also been further verified using SAED and TEM. The TEM bright field image, SAED pattern and EDX spectrum of an intermetallic phase in an Mg-Al-La alloy are shown in Figure 7. By indexing the SAED pattern the new $(\text{Al,Mg})_3\text{La}$ phase [33] has been identified and found to have a similar needle or plate-like morphology to the Al$_{11}$Ce$_3$ phase. The SAED data in combination with EDX also confirms that the polyhedral and eutectic acicular phases are Al$_5$La$_2$ and $(\text{Al,Si})_5\text{La}_2$, respectively, and the eutectic lamellar-like phase is Mg$_{12}$La. It is also worth mentioning that the Mg$_{12}$La morphology is in agreement with the observation reported in [36], but is different to the Mg$_{12}$Ce morphology in this study.
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A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Figure 6 Identification of intermetallic phases in sand-cast ALa44 by SEM-EDX analysis: (a) low-magnification backscattered electron image, (b) high-magnification backscattered electron image, (c) EDX spectrum of $(Al,Mg)_3La$, (d) EDX spectrum of $Mg_{17}Al_{12}$ and (e) EDX spectrum of $(Al, Si)_3La_2$. 
Chapter 8
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Figure 7 TEM bright field images, selected area electron diffraction patterns and EDX spectra of (Al,Mg)₃La phase in the as-cast ALa44 alloy.

Thermodynamic predictions for Mg-Al-Ce alloys

During the solidification of low Ce content alloys (ACe44 and ACe47), the solidification path moves toward the Al-RE region of the phase diagram. Using the Pandat® thermodynamic package and its PanMagnesium 2018 [35] database, both equilibrium and Scheil-Gulliver (non-equilibrium) predictions for ACe44 as well as the Scheil-Gulliver prediction for ACe47 (Table 2) indicate the presence of α-Mg, Al₁₁Ce₃ and Mg₁₇Al₁₂ phases in these alloys.

It is interesting to note that the ACe47 solidification path predicted by the equilibrium calculations is different from the predictions provided by the Scheil-Gulliver equation. According to the equilibrium predictions, the final phases in this alloy are α-Mg, Mg₁₂Ce and A₁₁Ce₃. In contrast, the Scheil-Gulliver prediction for this alloy indicates the formation of Mg₁₇Al₁₂ but not Mg₁₂Ce.
During the solidification of high Ce content alloys (ACe310 and ACe413), the solidification path moves toward the Mg-RE side of the phase diagram under equilibrium conditions. The final phases predicted using equilibrium calculations are $\alpha$-Mg, Mg$_{12}$Ce and Al$_{11}$Ce$_3$. However, solidification according to the non-equilibrium (Scheil-Gulliver) condition, as shown in Table 2, heads towards the Al-RE side of the phase diagram, where the final phases predicted are $\alpha$-Mg and Al$_2$Ce.

The temperature-fraction solid curves for the different Mg-Al-Ce alloys were modelled using the Scheil-Gulliver solidification simulation feature in Pandat®. The plots in Figure 8 indicate that these alloys have narrow solidification ranges. Figure 8 shows that an increase in the Ce content from 4 wt.% to 10 wt.% Ce results in a decrease in the liquidus temperature, when the alloy is hypo-eutectic. However, ACe413 is hyper-eutectic with Al$_2$Ce as the primary phase. In hypo-eutectic alloys, Al$_2$Ce is also present but forms as a part of a eutectic reaction which increases in temperature as the Ce content increases. Lastly, the solidus temperature ($\alpha$-Mg + Al$_{11}$Ce$_3$ + Mg$_{17}$Al$_{12}$) for ACe44 and ACe47 are similar but the solidus temperature of $\alpha$-Mg + Al$_2$Ce for ACe310 is higher than that in the ACe413 alloy.
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Figure 8 (a) Temperature-fraction solid curves generated using Scheil-Gulliver equation for Mg-Al-Ce alloys with varying Ce concentrations in the alloys. (b) Is the magnified plot of liquidus temperature ($L + \alpha$-Mg for ACe44, ACe47 and ACe310, whereas $L + Al_2Ce$ for ACe413), (c) Is the magnified plot of “$L + \alpha$-Mg + Al$_2$Ce” for ACe44, ACe47 and ACe310, whereas “$L + Al_2Ce + \alpha$-Mg” for ACe413, and (d) Is the magnified plot of “$\alpha$-Mg + Al$_{11}$Ce$_3 + Mg_{17}Al_{12}$” for ACe44 and ACe47, whereas “$\alpha$-Mg + Al$_2$Ce” for ACe410 and “Al$_2$Ce + $\alpha$-Mg” for ACe413.

Thermodynamic predictions for Mg-Al-La alloys

In Mg-Al-La alloys the solidification path moves toward the Mg-RE region of the phase diagram as the La content increases for both the equilibrium and Scheil-Gulliver predictions. At low La concentrations (ALa44), the predicted phases are $\alpha$-Mg + Al$_{11}$La$_3$ + Mg$_{17}$Al$_{12}$. As the La concentration increases in ALa37, Mg$_{12}$La and Al$_{11}$La$_3$ are predicted by the equilibrium calculation and only Al$_{11}$La$_3$ is predicted by the Scheil-Gulliver equation. As the La concentration continues to increase, Mg$_{12}$La and Al$_{11}$La$_3$ are predicted by the equilibrium calculation and Mg$_{12}$La and Al$_2$La is predicted by the Scheil-Gulliver equation to be present in the ALa311 and ALa413 alloys, as shown in Table 3.
Chapter 8  
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

Table 3 Final phases in the Mg-Al-La alloys predicted by equilibrium and Scheil-Gulliver equations using Pandat [35].

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<th>Equilibrium or Scheil predictions</th>
<th>Predicted final phases</th>
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The temperature-fraction solid curves for the Mg-Al-La alloys are shown in Figure 9. Similar to the Mg-Al-Ce alloys, these alloys also have narrow solidification ranges. In addition, increasing the La content from 4 wt.% to 13 wt.% is predicted to result in a decrease in the liquidus temperature. As the La content increases, the amount of the $\alpha$-Mg/Mg_{12}La eutectic phase increases. This is also in agreement with the microstructural observations (Figure 1).
Chapter 8
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys

![Figure 9](a) Temperature-fraction solid curves generated using Scheil-Gulliver equation for Mg-Al-La alloys with varying La concentrations in the alloys. (b) Is the magnified plot of liquidus temperature (L + α-Mg for all Mg-Al-La alloys). (c) Is the magnified plot of “L+α-Mg+Al₂La” for ALa44 and “α-Mg+Al₂La+Mg₁₂La” for ALa37, ALa311 and ALa413, and (d) Is the magnified plot of “α-Mg+Al₁₁La₃+Mg₁₇Al₁₂” for ALa44.

Discussion

Comparison of intermetallic phases in Mg-Al-Ce and Mg-Al-La alloys

In the present study, the observed morphology and microstructure (Figure 1) as well as the intermetallic phases (Figure 2 and Figure 5) in the Mg-Al-Ce alloys are different compared to those in the Mg-Al-La alloys. Table 4 provides a summary of the phases identified in the alloys investigated. In the Mg-Al-Ce alloys, the Al₅Ce₂ and Al₂Ce phases were present in all four alloys, whereas Al₁₁Ce₃ was only observed in the ACe44 and ACe47 alloys and Mg₁₂Ce in the ACe310 and ACe413 alloys. Compared to the Mg-Al-La alloys, (Al,Mg)₃La and Al₃La₂ phases are formed irrespective of the La content in the range studied, whereas the Mg₁₂La phase is only present in the ALa37, ALa311 and ALa413 alloys. The silicon-containing phases in the alloys are a consequence of the minor silicon impurity in the alloys.

It has been reported that the Mg₁₇Al₁₂ phase is often formed during slow cooling rate conditions, such as sand cast and permanent cast. However, Mg₁₇Al₁₂ is not observed in rapid solidification, such as high pressure die-cast, due to the supersaturation of aluminium in
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys magnesium during fast cooling [11]. This is in agreement with this study, where \( \text{Mg}_{17}\text{Al}_{12} \) is observed in the ACe44 and ALa44 alloys. There are no \( \text{Mg}_{17}\text{Al}_{12} \) observed in the higher RE-containing alloys due to the Al used up in the preferential reactions of Al and RE to form Al-RE intermetallic phases [37, 38].

Comparing the thermodynamic predictions between the two systems, the Scheil-Gulliver model predicted that the \( \text{Al}_{11}\text{Ce}_3 \) phase or the \( \text{Al}_{11}\text{La}_3 \) phase is the dominant intermetallic phase in low RE content alloys, such as ACe44 and ALa44, respectively. In this study, \( \text{Al}_{11}\text{Ce}_3 \) is observed in both ACe44 and ACe47. However, there is no \( \text{Al}_{11}\text{La}_3 \) phase found throughout the four sand-cast Mg-Al-La alloys in the present study, although this phase has been observed in high pressure die-cast ALa44 alloy which is presented elsewhere [28] (Chapter 7). \( \text{Al}_2\text{Ce} \) and \( \text{Al}_2\text{La} \) are the predicted intermetallic phases in high RE content alloys, such as ACe413 and

### Table 4 Summary of phases identified for the alloys in this study. O is for observations and P is for predictions from Pandat PanMg2018 database [35]. *only equilibrium * only Scheil-Gulliver.

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<th>ACe47-O</th>
<th>ACe47-P</th>
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</tbody>
</table>
A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys ALa413, respectively. However, the observations in this study show that Al$_2$Ce is present in all four Mg-Al-Ce alloys, but Al$_2$La is not observed in any of the Mg-Al-La alloys. There is also an additional Al$_3$La phase in the Mg-Al-La system database, but there is no equivalent phase in the Mg-Al-Ce system. It is worth mentioning that the Al$_3$La (currently in the database) is not the same as the (Al,Mg)$_3$La phase described in [33], although the chemical compositions of Al$_3$La and (Al,Mg)$_3$La are similar. The hexagonal Al$_3$La phase has a distinctly different crystal structure compared to the observed orthorhombic (Al,Mg)$_3$La phase, as reported in [33]. In addition, the thermal stability of the (Al,Mg)$_3$La phase is higher than the Al$_2$La and Al$_{11}$La$_3$ phases in the Mg-Al-La system, as reported in [28] (Chapter 7).

Another observation is that the Al$_2$Ce particles are found at the centre of magnesium grains from 7 wt.% of cerium and above (Figure 1). This suggests that the ACe47, ACe310 and ACe413 are all hyper-eutectic alloys. A previous study by the authors also indicated that ACe310 and ACe413 are hyper-eutectic [34]. In the Mg-Al-La alloys, however, the primary intermetallic particles (Al$_5$La$_2$) are not seen until the lanthanum concentration reaches 11 wt.% or more. The formation of different primary intermetallic phases in Mg-Al-Ce and Mg-Al-La alloys are detailed in previous studies by the authors [33, 34].

As the solidification process continues, the phase selection of the eutectics is also different between the Mg-Al-Ce and Mg-Al-La alloys. For low Ce content alloys (ACe44 and ACe47), the solidification tends to move towards the Al$_5$Ce$_2$/Al$_{11}$Ce$_3$ mono-variant eutectics. Whereas, in higher Ce content alloys (ACe310 and ACe413), the solidification ends in the Mg$_{12}$Ce phase and bypasses the formation of Al$_{11}$Ce$_3$. However, the solidification path for the lower La content alloys, such as the ALa44, heads toward the Al$_5$La$_2$ and (Al,Mg)$_3$La containing eutectic, but continues to Mg$_{12}$La as the La content increases (ALa37 and ALa311), and ends with very small amounts of the MgLa-containing eutectic at the highest La content (ALa413). Lastly, the proportion of eutectic is higher in the La content alloys compared with the Ce alloys with a similar concentration. Hence it is clear that the intermetallic phase(s) that form in the Mg-Al-Ce and Mg-Al-La alloys are different.

**Conclusions**

The microstructure of sand-cast Mg-Al-Ce and Mg-Al-La alloys have been characterised in this study. The intermetallic phases formed in the Ce-containing alloys and La-containing alloys are different. The key findings in this study are:
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- In the Mg-Al-Ce alloys, the primary intermetallic phase, Al\textsubscript{2}Ce, is found to be at the centre of the grains at Ce concentrations of 7 wt.% and above. This indicates that the ACe44 alloy is a hypo-eutectic alloy, whereas ACe47, ACe310 and ACe413 are all hyper-eutectic. On the other hand, the primary intermetallic phase, Al\textsubscript{5}La\textsubscript{2}, only appears in 11 wt.% La or more in the Mg-Al-La alloys (ALa311 and ALa413).

- The Al\textsubscript{11}Ce\textsubscript{3} eutectic phase forms in low Ce content alloys (ACe44 and ACe47), whereas the Mg\textsubscript{12}Ce eutectic phase forms in high Ce content alloys (ACe310 and ACe413). However, in Mg-Al-La alloys, Al\textsubscript{5}La\textsubscript{2} and (Al,Mg)\textsubscript{3}La containing eutectics are formed in ALa44, but in ALa37, ALa311 and ALa413 solidification continue to form the Mg\textsubscript{12}La eutectic phase. As the La content increases in ALa413, the MgLa phase is also found in the alloy.

Acknowledgements

This study was supported by the Australian Research Council (ARC) through linkage project LP130100828. The authors would like to thank Dr. Aaron Seeber of CSIRO for his time in providing useful advice and information on the XRD experiments. In addition, the authors wish to thank Mr. Gary Savage and Mr. Andrew Yob of CSIRO for their time in assisting the casting process as well as providing support throughout the casting experiments. The RMIT Microscopy and Microanalysis Facility (RMMF) as well as the Monash Centre for Electron Microscopy (MCEM) are acknowledged for the microstructure characterisation presented in this paper.
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References


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Chapter 8
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34. C. Wong, et al. Experimental study of the solidification microstructure in the Mg-rich corner of Mg–Al–Ce system. in TMS Annual Meeting & Exhibition. 2018. Springer.

35. CompuTherm, Pandat software and PanMagnesium 2018 thermodynamic database, Madison, Editor.


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Chapter 9

Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys

Charlotte Wong¹, Suming Zhu¹,², Trevor B. Abbott¹,², Mark J. Styles², Kazuhiro Nogita³, Mark A. Gibson¹,², Mark A. Easton¹

¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia
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Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys

Title
The influences of RE alloying element and cooling rate on the solidification microstructure of Mg-Al-La and Mg-Al-Ce alloys

Charlotte Wong¹, Suming Zhu¹,⁴, Ace Christopher Dacaya¹, Trevor B. Abbott¹,⁴,⁵, Mark J. Styles², Kazuhiro Nogita³, Mark A. Gibson¹,²,⁴, Mark A. Easton¹*
¹ School of Engineering, RMIT University, Carlton, Victoria 3053, Australia
² CSIRO Manufacturing, Clayton, Victoria 3168, Australia
³ School of Mechanical and Mining Engineering, University of Queensland, Brisbane, Queensland 4072, Australia
⁴ Department of Materials Science and Engineering, Monash University, Victoria 3800, Australia
⁵ Magontec Ltd, Sydney, New South Wales 2000, Australia

*Corresponding author: Mark Easton (Mark.Easton@rmit.edu.au)

Abstract
The effects of RE alloying elements and cooling rates on the solidification microstructure of Mg-Al-RE alloys were investigated. A series of Mg-Al-La and Mg-Al-Ce alloys were gravity cast into a wedge-shaped mould to achieve a gradient in cooling rate. Microstructural features, such as grain size and secondary dendrite arm spacing (SDAS), were analysed by optical microscopy and scanning electron microscopy. The relationship between the dendrite growth time and the SDAS was analysed by the commonly used empirical equation. In addition, microstructure-property relationships between yield stress and microstructure features (SDAS and grain size) for these alloys were discussed and established based on the Hall-Petch equation. Using the relationships developed in this study, it is possible to predict the microstructure features and yield stress at a given cooling rate for the investigated alloys.
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Introduction

Magnesium alloys have attracted interest in the automotive industry because of their low density and high specific strength, which makes them suitable for light weighting applications in vehicles to achieve substantial fuel savings [1, 2]. Mg-Al alloys are the most commonly used alloys in industry, including the Mg-Al-Zn (AZ) and Mg-Al-Mn (AM) series of alloys. However, these alloys tend to suffer from poor creep resistance and significant reduction in tensile strength at elevated temperatures [3], which limits their application to temperatures below 125 °C [4].

To further improve the elevated temperature properties of Mg alloys, one of the most effective approaches is the addition of rare earth (RE) elements. This allows the formation of high thermal stability intermetallic phases in preference to the less stable Mg\textsubscript{17}Al\textsubscript{12} phase [5-8]. Mg-Al-RE (AE) alloys, including AE42 and AE44, are currently used in commercial applications, such as engine crankcases, oil housings and oil pans [4, 9, 10]. Recent investigations have indicated that the addition of individual RE elements, such as lanthanum (La) and cerium (Ce) to Mg-Al alloys (AE alloys) can lead to the formation of different microstructures and hence possibly different mechanical properties of the alloys [11-13].

High pressure die-casting (HPDC) is still the prominent manufacturing process for magnesium components, representing the vast majority of applications of Mg alloys [14]. It is well known that the morphology of microstructure and intermetallic phases have an important influence on the properties of the alloys [15]. Solidification behaviour is critical, especially in the die-casting process, because it determines the final microstructure morphology, such as secondary dendrite arm spacing (SDAS) and grain size, which affects the properties of the alloys [16-20].

Grain size and SDAS decrease with increased cooling rate [21, 22]. The average grain size and SDAS have a direct influence on the mechanical properties, such as the yield stress and hardness. The relationship between yield strength or flow stress and grain size is often described by the Hall-Petch equation (Equation 1) [23]. In alloys with dendritic grain morphologies, often the SDAS can be the microstructural parameter that is important in controlling the strength (Equation 2) [24, 25].

\[
\sigma = \sigma_0 + kd^{-1/2} \quad [1]
\]

\[
\sigma = \sigma_0 + h\lambda_2^{-1/2} \quad [2]
\]
Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys

where $\sigma_0$ is the intercept stress, also known as the friction stress when dislocations move on the slip plane, whereas $k$ and $h$ are the Hall-Petch coefficients, which represents the stress concentration factor. $d$ is the average grain size and $\lambda_2$ is the average secondary dendrite arm spacing (SDAS).

The SDAS ($\lambda_2$) is often described by the simple empirical equation [26, 27],

$$\lambda_2 = M t_f^n$$  \[3\]

where $t_f$ is the solidification time range between the liquidus and solidus, $n$ is often between 0.33 and 0.5, and $M$ is a fitting factor, which is dependent on the alloy elemental concentration [26, 28, 29] and constituents [30]. Equation 3 can be modified to relate the SDAS with the pre-solidification cooling rate, using [26]:

$$\lambda_2 = M_2 \dot{T}^{-n}$$  \[4\]

where $\dot{T}$ is the pre-solidification cooling rate (or the instantaneous cooling rate at liquidus) and $M_2$ is a modified fitting factor for a particular alloy.

Thermal analysis, such as computer-aided cooling curve analysis (CA-CCA), is a common approach to investigate the solidification behaviour of alloys [31, 32] and is used in this study to assess the solidification behaviour of AE alloys at different cooling rates and RE concentrations. The effect of cooling rates and RE concentrations, which determine the cast microstructure and the solidification behaviour, were studied with a goal of understanding their influence on microstructural features. The purpose of the present study is then to characterise the effect of cooling rate on the microstructure of Mg-Al-RE alloys and develop a relationship between the morphological features and mechanical properties.

**Methodology**

**Sample preparation**

The nominal compositions of the alloys investigated in this study were Mg-4Al-4La (ALa44), Mg-4Al-4Ce (ACE44), Mg-4Al-13Ce (ACE413) and Mg-4Al-13La (ALa413) (all compositions in weight percent unless otherwise specified). To prepare these alloys, pure elemental magnesium (99.95 %), aluminium (99.9 %), lanthanum (99.9 %) and cerium (99.5 %) ingots were alloyed under an inert cover gas, which is a mixture of nitrogen and R134a refrigerant gas. The alloys were stirred well after each addition, to ensure complete mixing. The alloy was then cast into a preheated wedge mould, which consists of two parts: a permanent
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mould and sand mould. The wedge mould was preheated and removed from the oven when the mould temperature reached approximately 120 °C. The molten alloy was poured into the mould when the mould temperature cooled to approximately 95 °C. The pouring temperature of the molten metal into the mould was 720 °C for ALa44 and ACe44 alloys and 800 °C for ALa413 and ACe413 alloys. The molten alloys were solidified to room temperature before removing them from the mould. The chemical compositions of the alloys were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Table 1).

*Table 1 Chemical analysis using ICP-AES and the designed compositions of the investigated alloys (wt.%).*

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Chemical analysis</th>
<th>Nominal compositions</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La</td>
<td>Ce</td>
</tr>
<tr>
<td>ALa44</td>
<td>3.81</td>
<td>&lt;0.005</td>
</tr>
<tr>
<td>ACe44</td>
<td>&lt;0.005</td>
<td>3.87</td>
</tr>
<tr>
<td>ACe413</td>
<td>&lt;0.005</td>
<td>13.1</td>
</tr>
<tr>
<td>ALa413</td>
<td>13.4</td>
<td>0.005</td>
</tr>
</tbody>
</table>

**Thermal analysis**

To obtain the cooling curves during solidification, computer-aided cooling curve thermal analysis (CA-CCA) of the investigated alloys was undertaken by casting the wedge samples with thermocouples embedded in the mould such that they were in direct contact with the molten alloy. By casting into a wedge, it is possible to produce a range of cooling rates in one casting. The details of the mould and thermocouple positions are illustrated in Figure 1.

Seven K-type stainless steel MI (mineral insulated) thermocouples were placed at different positions in the mould (Figure 1) before pouring the molten alloy into the mould to measure the cooling rates. The time interval for the temperature measurements was 0.1 s. These thermocouples were monitored using a high-speed data acquisition system. The temperature signal was recorded continuously with a Picolog data logger, and the temperature data was translated into a cooling curve through the Picolog recorder software. The reproducibility of the individual measurements from the thermocouples was confirmed by repetition. X-ray radiographs were collected from the solidified samples to verify the locations of the
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thermocouples. The cooling curve (T-t) and its first derivative curve (dT/dt-t) were plotted using Picolog and Origin software.

As expected, location 1 at the tip of the wedge has the fastest cooling rate, whilst location 7 has the slowest cooling rate. In this study, the following cooling parameters were calculated: instantaneous cooling rate (at liquidus) and dendrite growth time (time interval between the start of solidification and the point where the dendrite arms begin to demarcate and restrict further coarsening by intermetallic particles). The average instantaneous cooling rate at liquid obtained at the seven thermocouple locations ranged between 8 °C/s and 80 °C/s for all alloys. However, direct measurements were difficult in positions 1 and 2, and so the cooling rates at these positions were obtained using extrapolation. The dendrite growth time varies between alloys due to the difference in alloy compositions. These cooling curves provide details about the characteristic features of the solidification path of the experimental alloys.

![Diagram of wedge mould dimensions and thermocouple positions](image)

*Figure 1 Schematic of the wedge mould dimensions and thermocouple positions in the wedge cast sample.*

**Microstructure analysis and hardness test**

For microstructural examination, samples were cut from the regions near each thermocouple tip at seven locations along each wedge casting. The samples were ground to approximately 15 µm using silicon carbide paper with a grit size of 500. After grinding, the samples were then polished with diamond and finished with alumina suspension to approximately 0.04 µm
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Particle size. The samples were ultrasonically cleaned for 180 seconds after each step of grinding and polishing.

In this study, the microstructural features, in particular the secondary dendrite arm spacing (SDAS) and grain size were measured. To measure the grain size, the samples were etched using an acetic-picric acid solution and viewed under polarised light to observe the grain contrast using an optical microscope. The ASTM Standard E112-13 linear intercept method was used to measure the SDAS and grain size. The SDAS was measured by determining the number of arms that intercept a straight line of a known length from SEM micrographs. Approximately 70 secondary dendrite arms close to the thermocouple position in the wedge were counted and averaged in each alloy. To determine the grain size, a linear pattern was drawn over the grains allowing the grain boundaries to be counted whenever they intercepted one of the lines. 50-100 grain boundaries were measured. The solidification microstructures were also observed using a scanning electron microscope (FEI Quanta 200 ESEM) equipped with energy dispersive X-ray spectroscopy (Oxford Instruments X-MaxN 20) at 25 kV.

Intermetallic phase fractions were measured from the SEM micrographs using image analysis technique, ImageJ [33]. The SEM images were converted into binary images with only black and white to distinguish the contrast between α-Mg and intermetallic/eutectic phase. At least three SEM images were analysed.

Hardness at each of the seven locations of the wedge samples was measured using a Micromet® 5104 micro-indentation hardness tester with a load between 100 gf and 200 gf. No fewer than 5 indentations were measured and averaged for each location of the wedge samples.

Results

Cooling curve analysis for Mg-Al-Ce and Mg-Al-La alloys

The cooling curves and the first derivative curves of the four investigated alloys (ACe44, ACe413, ALa44 and ALa413) at seven locations along the wedge castings (as measured from the wedge tip, Figure 1) were used to determine the instantaneous cooling rate (at liquidus) and freezing time (dendrite growth time). Typical cooling curves for one of the four investigated alloys are shown in Figure 2. The measured cooling rates for these alloys are shown in Figure 3 and the data for the lines of best fit in this figure are shown in Table 2.
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It is worth noting that the first derivative curves improve the accuracy of determining characteristic points of a solidification process, such as the start and end of a process that may be difficult to observe directly from the cooling curves. Hence, the first derivatives of the cooling curves were employed to aid with determining the cooling rates in this study.

![Cooling curves at different locations along the wedge cast](image)

*Figure 2 Cooling curves at different locations along the wedge cast, as measured from the wedge tip, for ALa413. Thermocouple location 1 is located at 10 mm, location 2 is at 30 mm, location 3 is at 70 mm, location 4 is at 90 mm, location 5 is at 115 mm, location 6 is at 150 mm and lastly location 7 is at 165 mm, measured from the tip of the wedge cast.*
Figure 3 (a) Instantaneous cooling rate at liquidus ($\dot{T}$) and (b) dendrite growth time ($t_f$) of the investigated alloys at different wedge locations. The numbers above indicate the locations within the wedge casting. The instantaneous cooling rate at liquidus at location 1 was estimated using the extrapolation method, whereas the cooling rates at the remaining locations were measured directly from the experimental cooling curves.
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Table 2 Data for lines of best fit in Figure 3 to the equations of (a) instantaneous cooling rate at liquidus and (b) dendrite growth time as a function of wedge distance. (*where  \( \dot{T} \) is the instantaneous cooling rate at liquidus (°C/s), \( t_f \) is dendrite growth time (s) and \( D \) is wedge distance (mm)).

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Figure 3(a): instantaneous cooling rate at liquidus</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>( \dot{T} = -0.466D + 79.58 )</td>
<td>0.97</td>
</tr>
<tr>
<td>ALa44</td>
<td>( \dot{T} = -0.435D + 74.79 )</td>
<td>0.96</td>
</tr>
<tr>
<td>ACe413</td>
<td>( \dot{T} = -0.495D + 85.70 )</td>
<td>0.97</td>
</tr>
<tr>
<td>ALa413</td>
<td>( \dot{T} = -0.537D + 94.27 )</td>
<td>0.94</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Figure 3(b): dendrite growth time</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>( t_f = 0.298e^{0.032D} )</td>
<td>0.99</td>
</tr>
<tr>
<td>ALa44</td>
<td>( t_f = 0.518e^{0.030D} )</td>
<td>0.98</td>
</tr>
<tr>
<td>ACe413</td>
<td>( t_f = 0.100e^{0.038D} )</td>
<td>0.99</td>
</tr>
<tr>
<td>ALa413</td>
<td>( t_f = 0.236e^{0.034D} )</td>
<td>0.98</td>
</tr>
</tbody>
</table>

The cooling rate obtained at location 1 of the wedge casting was determined by linear extrapolation, assuming that there is a linear relationship between cooling rate and the distance from the wedge tip. Because the tip of the wedge mould (location 1) is very narrow and the responsiveness of the thermocouple is limited, the peak temperature measured was only 400 °C, which means that the “pre-solidification” cooling rate could not be measured directly. This assumption of a linear relationship between cooling rate and the distance from the wedge tip is reasonable given that the SDAS and grain size both increase linearly as the cooling rate decreases, including the transition from the permanent mould to sand mould (location 4 and 5). The SDAS and grain size will be discussed in the subsequent sections.

The solidification time at each thermocouple location in the wedge castings were also obtained in this study using the thermal analysis data. The solidification sequence, as well as the liquidus and solidus temperatures predicted using Pandat, were used to interpret the characteristic points on the cooling curves, which are marked with different numbers as shown in Figure 4. The solidification process starts with point “1”, which refers to the start of solidification of the primary phase (liquidus), point “2” represents the beginning of the eutectic reaction and the formation of secondary phases as part of eutectic reactions, and point “3” represents the end of solidification (solidus).
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Figure 4 Cooling curve obtained at location 7 of ALa44 showing the different stages of solidification.

The solidification time (freezing time), also called the dendrite growth time, measured in this study is defined as the time to solidify the alloy from the start of solidification (point 1, liquidus) to its point 2 in Figure 4. This is where the intermetallic phase particles, formed during eutectic reactions, are beginning to demarcate the dendrite arms and restrict further coarsening [26]. Pandat was used as a guide to determine the solidification sequence of the alloys (Table 3) and the reaction corresponding to point 2 is marked by an “*”. However, it has been noted that the observed solidification sequence is different from that of the Pandat predictions; this is especially clear in the Mg-Al-La system [34]. Whilst investigations are ongoing into characterising the solidification sequence of these alloys, in particular trying to understand the phase evolution, the point at which the dendrites are expected to stop coarsening was determined by identifying point 2 on the cooling curve as seen in Figure 4.
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Table 3 Solidification sequence and temperature predicted by Scheil-Gulliver equation using Pandat [35] for ACE44, ALa44 and ACe413, whereas solidification sequence and associated temperature for ALa413 is determined by [34].

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Solidification sequence</th>
<th>Fraction Solid</th>
<th>Temperature (˚C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>L $\rightarrow$ L + $\alpha$-Mg</td>
<td>0.62</td>
<td>624</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg $\rightarrow$ L + $\alpha$-Mg + Al$_2$Ce</td>
<td>0.97</td>
<td>593*</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg + Al$<em>2$Ce $\rightarrow$ L + $\alpha$-Mg + Al$</em>{11}$Ce$_3$</td>
<td>0.99</td>
<td>562</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg + Al$<em>{11}$Ce$<em>3$ $\rightarrow$ $\alpha$-Mg + Al$</em>{11}$Ce$<em>3$ + Mg$</em>{17}$Al$</em>{12}$</td>
<td>1.00</td>
<td>436</td>
</tr>
<tr>
<td>ACe413</td>
<td>L $\rightarrow$ L + Al$_2$Ce</td>
<td>0.01</td>
<td>634</td>
</tr>
<tr>
<td></td>
<td>L + Al$_2$Ce $\rightarrow$ L + Al$_2$Ce $+$ $\alpha$-Mg</td>
<td>0.99</td>
<td>604*</td>
</tr>
<tr>
<td></td>
<td>L + Al$_2$Ce + $\alpha$-Mg $\rightarrow$ Al$_2$Ce + $\alpha$-Mg</td>
<td>1.00</td>
<td>564</td>
</tr>
<tr>
<td>ALa44</td>
<td>L $\rightarrow$ L + $\alpha$-Mg</td>
<td>0.66</td>
<td>623</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg $\rightarrow$ L + $\alpha$-Mg + Al$_2$La</td>
<td>0.92</td>
<td>585</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg + Al$_2$La $\rightarrow$ L + $\alpha$-Mg + Al$_3$La</td>
<td>0.96</td>
<td>570*</td>
</tr>
<tr>
<td></td>
<td>L + $\alpha$-Mg + Al$<em>3$La $\rightarrow$ L + $\alpha$-Mg + Al$</em>{11}$La$_3$</td>
<td>0.99</td>
<td>551</td>
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<tr>
<td></td>
<td>L + $\alpha$-Mg + Al$<em>{11}$La$<em>3$ $\rightarrow$ $\alpha$-Mg + Al$</em>{11}$La$<em>3$ + Mg$</em>{17}$Al$</em>{12}$</td>
<td>1.00</td>
<td>436</td>
</tr>
<tr>
<td>ALa413</td>
<td>L $\rightarrow$ L + Al$_3$La$_2$</td>
<td>-</td>
<td>630</td>
</tr>
<tr>
<td></td>
<td>L + Al$_3$La$_2$ $\rightarrow$ L + Al$_3$La$_2$ $+$ $\alpha$-Mg</td>
<td>-</td>
<td>617</td>
</tr>
<tr>
<td></td>
<td>L + Al$_3$La$_2$ + $\alpha$-Mg $\rightarrow$ L + Al$_3$La$<em>2$ $+$ $\alpha$-Mg + Mg$</em>{17}$La$_2$</td>
<td>-</td>
<td>609*</td>
</tr>
<tr>
<td></td>
<td>L + Al$_3$La$<em>2$ + $\alpha$-Mg + Mg$</em>{17}$La$_2$ $\rightarrow$ Al$_5$La$<em>2$ + $\alpha$-Mg + Mg$</em>{17}$La$_2$ + (Al,Mg)$_3$La</td>
<td>-</td>
<td>602</td>
</tr>
</tbody>
</table>

The as-cast microstructure of Mg-Al-Ce and Mg-Al-La alloys

Typical optical micrographs of one of the four investigated alloys are shown in Figure 5. The solidification microstructures of the alloys are presented in Figure 6. It is evident that the microstructure (grain size and SDAS) in both the Mg-Al-Ce and Mg-Al-La alloys becomes coarser as the cooling rate decreases from position 1 to position 7. In addition, there appears to be a greater fraction of eutectic in the Mg-Al-La alloys, compared with the Mg-Al-Ce alloys, as the RE concentration increases.
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Figure 5 Optical images of ACe44 at location (a) 2, (b) 3, (c) 4, (d) 5, (e) 6 and (f) 7, used for grain size measurement.

Figure 6 SEM images of (a) ACe44, (b) ACe413, (C) ALa44 and (d) ALa413 at different cooling rates along the wedge cast sample.
Comparing images in the vertical direction in Figure 6, it is noticed that the change in cooling rate along the wedge affects not only the morphology of the $\alpha$-Mg but also the second phase development in the alloy. This can be seen clearly in ACe44 as there is an additional bright particle phase, commonly identified as Al$_2$Ce (identified in Chapter 8), found predominantly near the centre of the grains as the cooling rate decreases from location 1 to location 2. This phase is more prominent as the cooling rate continues to decrease along the wedge. A similar observation can be made in the ALa413 alloy. However, there are two additional phases that appear later in this alloy at position 4; these phases include bright intermetallic particles (Al$_5$La$_2$) and smaller blocky or irregular eutectic structure ((Al,Mg)$_3$La), as previously identified in [34, 36] (Chapter 5 and 6). In comparison, very few bright particles are observed in the ALa44 alloy at any location along the wedge, whereas bright Al$_2$Ce particles are observed at all locations along the ACe413 wedge. In addition, the fraction of the bright particles is greater in the Mg-Al-Ce alloys than the Mg-Al-La alloys, especially in the ACe413 alloy.

It can also be seen in Figure 6 that the amount of eutectic phase increases as the Ce or La concentration increases from 4 wt.% to 13 wt.% in the respective alloy systems. The phase formation and their morphology are also different between the Mg-Al-Ce and Mg-Al-La alloys. Al$_2$Ce and Al$_5$Ce$_2$ are present in ACe44 and ACe413 alloys, whereas the eutectic Al$_{11}$Ce$_3$ only appears in ACe44. As the Ce content increases, the solidification moves towards the eutectic Mg$_{12}$Ce in ACe413. In the Mg-Al-La alloys, (Al,Mg)$_3$La and Al$_5$La$_2$ are present in ALa44 and ALa413, but the eutectic Mg$_{12}$La is only present in ALa413. Detailed microstructural examination of the Mg-Al-Ce and Mg-Al-La alloys can be found in Chapter 7 and 8.

**Relating the processing conditions to the microstructure**

Grain size and SDAS are critical features in the as-cast microstructure because they affect the mechanical properties of the alloy. Previous studies [17, 37-39] have proven that a decrease in the size of these features in Al and Mg alloys results in improvements in mechanical properties, often both strength and ductility. It is well known that the grain size and SDAS reduce with increased cooling rate during solidification. The alloy composition also changes the SDAS [26], such that an increase in RE concentration in the alloys can result in a reduced solidification interval (between liquidus and eutectic), decreasing the solidification time and hence the SDAS.

The grain size of the investigated alloys is plotted against the instantaneous cooling rate at liquidus in Figure 7. As expected the grain size is substantially refined towards the tip of the
Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys wedge due to rapid solidification. Alloys with 13 wt.% RE have much smaller average grain sizes compared to alloys with 4 wt.% RE. In addition, the Mg-Al-Ce alloys show smaller grain size measurements compared to Mg-Al-La alloys with ACe413 showing the smallest grain size.

Figure 7 The relationship between grain size and instantaneous cooling rate at liquidus for the four alloys.

Apart from the grain size, the variation in SDAS (measured close to the seven thermocouple locations) with the change of instantaneous cooling rate at liquidus and dendrite growth time for all four investigated alloys are shown in Figure 8(a) and (b), respectively. The data in Figure 8 were fitted to Equations 3 and 4 and the fitted values for the parameters of $M$, $M_2$ and $n$ are summarised in Table 4. For ACe44, the SDAS varies from around 6 µm at location 1 up to about 44 µm at location 6, and from approximately 4 µm at location 1 up to approximately 35 µm at location 7 for the ACe413 alloy. The Mg-Al-La alloys, correlate very closely with the Mg-Al-Ce alloys for the same alloy content, with the Mg-Al-La alloys possibly having a slightly smaller SDAS.
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Figure 8 SDAS as a function of (a) dendrite growth time for the alloys (Equation 3) and (b) instantaneous cooling rate at liquidus (Equation 4).

*Figure 8 SDAS as a function of (a) dendrite growth time for the alloys (Equation 3) and (b) instantaneous cooling rate at liquidus (Equation 4).*
In simple alloys the SDAS is related to the freezing range of the alloy, as it is proportional to the freezing time, $t_f$, in Equation 3. However, in more complex alloy systems the constant $M$ in Equation 3 is a function of the alloy composition [40, 41] and it has been shown that most of the coarsening occur in the early stages of solidification [42] as eutectic reactions will freeze in the SDAS by demarcating the dendrites. In other words, once the primary solidification of the $\alpha$-Mg is completed little further coarsening of the SDAS is likely to occur. Therefore, in this study, the dendrite growth time determined between liquidus and point 2 in Figure 4, as discussed in the previous section, is used to relate to the measured SDAS because this is considered to be more accurate from a theoretical perspective described in Equation 3 (where $t_f$ is the dendrite growth time in this study). On the other hand, the instantaneous cooling rate at liquidus (pre-solidification) can also be related to the measured SDAS, as described in Equation 4 (where $\dot{T}$ is the instantaneous cooling rate at liquidus in this study), because it is an independent experimental parameter that is directly related to the processing conditions and not substantially affected by the alloy composition.

The intermetallic phase fractions were also determined from the SEM micrographs (Figure 6). The measured intermetallic fractions are plotted with the instantaneous cooling rate at liquidus and the dendrite growth time, as shown in Figure 9. In general, the intermetallic phase fraction, especially the eutectic phase, increases with the cooling rate, which can also be seen in Figure 6. The data also shows that the intermetallic phase fraction increases with increasing RE
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content in the alloy. This is in agreement with other observations in Mg-Al and Mg-Zn alloys [37, 43, 44].

![Diagram](image)

**Figure 9** The relationship between intermetallic fraction and (a) instantaneous cooling rate at liquidus and (b) dendrite growth time for all alloys.
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Mechanical properties of the alloys

The hardness of these alloys at the seven positions is shown in Figure 10. The hardness test shows that the ACe413 alloy has a median hardness of approximately 102 HV at the tip of the wedge casting, and the ACe44 alloy only achieves a median hardness of approximately 68 HV at the same location. The increase in Ce concentration in the alloy from 4% to 13% results in approximately a 50% increase in hardness. Similar to the Mg-Al-Ce alloys, ALa413 exhibits a much greater median hardness than the ALa44 alloy; approximately 140 HV compared to approximately 72 HV for the ALa44 alloy. The trend in Figure 10 shows that the increase of RE content in the alloys can translate into an increase in hardness. It is interesting that the ALa413 alloy shows the highest hardness although the grain size is not the smallest among the four alloys as reported in the previous section.

![Hardness at each of the seven locations of the wedge samples for all four investigated alloys.](image)

The relationship between the hardness and grain size as well as SDAS is shown in Figure 11. Using the experimental data, the hardness values have been related to the proof stress in a range of magnesium alloys using [45], as shown in Equation 5.

\[
\text{Proof Stress} = 2.22 \times (HV) - 38.73
\]  

[5]
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where the proof stress is at 0.2 % strain and HV is the Vickers Pyramid Number. The estimated proof stress obtained from Equation 5 using the measured hardness were then plotted against grain size \( (d^{1/2}) \) and SDAS \( (\lambda_2^{1/2}) \), as shown in Figure 12. Parameters for the lines of best fit through the data are given in Table 5 and are used to compare with the Hall-Petch equation in Equation 1 and 2.

(a) Hardness versus Grain Size

![Graph showing hardness versus grain size](image1)

(b) Hardness versus SDAS

![Graph showing hardness versus SDAS](image2)

Figure 11: The relationship between hardness and (a) grain size as well as (b) SDAS.
Figure 12 Hall-Petch relationship using yield strength as a function of (a) grain size and (b) SDAS for all four investigated alloys, in which the yield strength was calculated using Equation 5.
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Table 5 Data for lines of best fit to Figure 12 using Hall-Petch relationship, Equation 1 and 2.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Relationship</th>
<th>R² Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 12(a) - data for lines of best fit to Equation 1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALa44</td>
<td>$\sigma_{ys} = 42.002 + 928.52/\sqrt{d}$</td>
<td>0.85</td>
</tr>
<tr>
<td>ALa413</td>
<td>$\sigma_{ys} = -6.264 + 2790.4/\sqrt{d}$</td>
<td>0.94</td>
</tr>
<tr>
<td>ACe44</td>
<td>$\sigma_{ys} = 46.081 + 653.02/\sqrt{d}$</td>
<td>0.58</td>
</tr>
<tr>
<td>ACe413</td>
<td>$\sigma_{ys} = 28.228 + 968.15/\sqrt{d}$</td>
<td>0.35</td>
</tr>
<tr>
<td>Figure 12(b) - data for lines of best fit to Equation 2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ALa44</td>
<td>$\sigma_{ys} = 51.157 + 202.65/\sqrt{\lambda_2}$</td>
<td>0.90</td>
</tr>
<tr>
<td>ALa413</td>
<td>$\sigma_{ys} = 91.707 + 260.69/\sqrt{\lambda_2}$</td>
<td>0.66</td>
</tr>
<tr>
<td>ACe44</td>
<td>$\sigma_{ys} = 60.585 + 135.49/\sqrt{\lambda_2}$</td>
<td>0.84</td>
</tr>
<tr>
<td>ACe413</td>
<td>$\sigma_{ys} = 78.164 + 210.81/\sqrt{\lambda_2}$</td>
<td>0.50</td>
</tr>
</tbody>
</table>

The hardness increases as the intermetallic fraction increases, as shown in Figure 13. ALa413 contains the greatest amount of intermetallic/eutectic; this is especially clear at the faster cooling rate, i.e. location 1 of the wedge casting. It appears the amount of intermetallic is greater in the Mg-Al-La alloys than the Mg-Al-Ce alloys at the same cooling rate and RE content. Hence, the amount of intermetallic/eutectic can also contribute significantly to the hardness, as also mentioned in [46].

![Figure 13 Plot of hardness against the amount of intermetallic phase in area fraction.](image)
Discussion

Effect of alloying content and cooling rate on the microstructure

The microstructure features, in particular the grain size and SDAS, vary significantly with the change in cooling rate and alloying concentration. The grain size at the same position is smaller for the Ce-containing alloys than the La-containing alloys. This is likely to be related to the nucleant potency of the polyhedral intermetallic particles, often identified as \( \text{Al}_2\text{Ce} \) in the Mg-Al-Ce alloys and \( \text{Al}_5\text{La}_2 \) in the Mg-Al-La alloys [34]. \( \text{Al}_2\text{Ce} \) particles have been identified as potent nucleants for magnesium grains previously [18, 47, 48], whereas the \( \text{Al}_5\text{La}_2 \) particles are less potent for magnesium grains [34]. Hence the grain size in the Mg-Al-Ce alloys is comparatively finer than that observed in Mg-Al-La alloys under similar solidification conditions [34].

The liquidus and solidus temperatures reduce as the cooling rate increases due to the kinetics of diffusion in both the liquid and solid [49, 50]. This facilitates an increased number density of intermetallic particles, such as \( \text{Al}_2\text{Ce} \), with increasing cooling rate [51]. This can be seen in Figure 5 and Figure 6, with ACe413 clearly showing a high number density of bright \( \text{Al}_2\text{Ce} \) particles. As these particles act as active nucleants for magnesium grains, the grain size decreases as a result of the increasing number of active nucleants at high cooling rates.

The observations in this study also indicate that the SDAS is not affected much by the selection of individual RE alloying elements for the same cooling rate; however the SDAS is finer when the RE alloying content increases from 4 wt.% to 13 wt.% This is because the high RE content alloys (ACe413 and ALa413) are hyper-eutectic as discussed in Chapters 4 [47], 6 [34] and 8, the freezing range for the formation of \( \alpha \)-Mg for these alloys is reduced, reducing the time for SDAS coarsening.

On the other hand, the refinement of SDAS at higher cooling rates is evident in this study. SDAS is often influenced by coarsening phenomena, which is controlled by the constitutional supercooling and diffusion time [26]. The increase in constitutional supercooling due to high cooling rates generates more secondary dendrite arms [52]. Furthermore at high cooling rates, the solid-liquid interface moves faster [52, 53]. Hence, the coarsening of SDAS can be restricted earlier by the enrichment of solute [26], during the solidification process. In addition, the diffusion rate reduces as the cooling rate increases. This means the rate of solute segregation is dependent on cooling rates. During the growth process, the composition at the dendritic surface varies, which results in solute diffusion from high solubility to low solubility. This
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process also causes dissolution of finer dendritic arms and coarsens other dendritic arms. During rapid cooling, diffusion is limited and hence SDAS is refined.

The relationship between SDAS and processing parameters, such as freezing time (dendrite growth time) and the instantaneous cooling rate at liquidus for these alloys can be developed using Equation 3 and 4. These equations in the logarithmic form are used to determine the $M$ and $n$ values for these alloys. The $n$ values obtained from Equation 3 using dendrite growth time (Table 4(a)) falls within the expected range of 0.33 and 0.5 [26, 27]. However, the $n$ values obtained from Equation 4 using the instantaneous cooling rate at liquidus (Table 4(b)) are above the expected range. Given that the $n$ values are within the expected range using the dendrite growth time, the relationship between the SDAS and dendrite growth time developed in this study can be used as guidance for SDAS predictions for these alloys if the cooling parameters are known. A summary of these equations is listed in Table 6.

Table 6 A summary of the relationship between SDAS and dendrite growth time (Equation 3) as well as the instantaneous cooling rate at liquidus (Equation 4) for all alloys.

<table>
<thead>
<tr>
<th>Type of alloys</th>
<th>$\lambda_2 = Mt^n$</th>
<th>$\lambda_2 = M_2T^n$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>$\lambda_2 = 9.8t^{0.39}$</td>
<td>$\lambda_2 = 203.2T^{-0.73}$</td>
</tr>
<tr>
<td>ACe413</td>
<td>$\lambda_2 = 7.1t^{0.39}$</td>
<td>$\lambda_2 = 238.8T^{-0.91}$</td>
</tr>
<tr>
<td>ALa44</td>
<td>$\lambda_2 = 11.2t^{0.37}$</td>
<td>$\lambda_2 = 328.9T^{-0.79}$</td>
</tr>
<tr>
<td>ALa413</td>
<td>$\lambda_2 = 5.6t^{0.35}$</td>
<td>$\lambda_2 = 196.8T^{-0.85}$</td>
</tr>
</tbody>
</table>

Effect of microstructure on alloy properties

It is concluded that the hardness at the tip of the wedge cast (location 1) is at its highest when compared to any other part of the sample for the same RE composition. This is due to the fast solidification rate at the tip of the wedge cast, leading to smaller average grain size and SDAS as well as higher intermetallic fraction.

Previously, it has been mentioned that the Hall-Petch relationship is effective at predicting yield stress, using both the SDAS and grain size for Mg alloys [54], this is in agreement with this study given that the $\sigma_0$, $k$ and $h$ values are positive as shown in Figure 12 and Table 5, except the $\sigma_0$ value obtained in the Hall-Petch relationship using the grain size in ALa413 results in a negative value, as shown in Figure 12(a). Hence, the Hall-Petch relationship
Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys developed in this study can be used as guidance in yield stress predictions specifically for these alloys. A summary of the relationship equations is listed in Table 7.

**Table 7** A summary of the Hall-Petch relationship between yield stress and (a) grain size, and (b) SDAS.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>(a) $\sigma = \sigma_0 + k d^{-1/2}$</th>
<th>(b) $\sigma = \sigma_0 + h \lambda_2^{-1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe44</td>
<td>$\sigma = 46.081 + 653.02d^{-1/2}$</td>
<td>$\sigma = 60.585 + 135.49\lambda_2^{-1/2}$</td>
</tr>
<tr>
<td>ACe413</td>
<td>$\sigma = 28.228 + 968.15d^{-1/2}$</td>
<td>$\sigma = 78.164 + 210.81\lambda_2^{-1/2}$</td>
</tr>
<tr>
<td>ALa44</td>
<td>$\sigma = 42.002 + 928.52d^{-1/2}$</td>
<td>$\sigma = 51.157 + 202.65\lambda_2^{-1/2}$</td>
</tr>
<tr>
<td>ALa413</td>
<td>$\sigma = -6.264 + 2790.4d^{-1/2}$</td>
<td>$\sigma = 91.707 + 260.69\lambda_2^{-1/2}$</td>
</tr>
</tbody>
</table>

The yield stress obtained using the microstructure-property relationships in Table 7(a) for ACe44 and ALa44 at the tip of the wedge (location 1) are 107 MPa and 127 MPa, respectively. Whereas, the yield stress obtained from the equations in Table 7(b) for ACe44 and ALa44 at the tip of the wedge are 117 MPa and 125 MPa, respectively. These calculated values are compared with [55], in which the HPDC ACe44 has a yield strength of 129 MPa and HPDC ALa44 has a yield strength of 134 MPa. Because the microstructure from HPDC is similar to those at the tip of the wedge gravity casting, location 1 is considered to be the more accurate position for comparison. Compared to the yield strength in [55], the estimated yield stress using the equations developed in this study is within 20% for the ACe44 and 10% for the ALa44.

Although the grain size in ACe413 is smaller than that in the ALa413 alloy, as mentioned in the results section, it is interesting that the ALa413 alloy has the highest hardness among the four alloys as observed in Figure 12. The Hall-Petch relationship can predict the strength of ALa44, ACe44 and ACe413 alloys in which smaller grain size leads to higher hardness and yield stress. However, ALa413 alloy does not follow this trend given in that it does not have the smallest grain size, but it has the highest hardness among the four alloys.

This observation can be explained by a large amount of eutectic in ALa413 (Figure 9). In addition, the area fractions of grains available in this alloy are relatively lower than other alloys due to the high volume of the eutectic. The high volume of eutectic, smaller eutectic spacing and lower number of grains in the ALa413 alloy can all be factors that are impacting on the hardness. In this study, it is believed that the grain size is the main influence on the hardness for ACe44, ACe413 and ALa44 alloys, although there are other factors, such as the SDAS, eutectic volume fraction and eutectic spacing, involved. However, the observation of the
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microstructure and the hardness in ALa413 alloy could further support the fact that the intermetallic fraction and SDAS have greater contributions to the hardness in this alloy.

Other than the mentioned possibilities, the $k$ value in the Hall-Petch relationship (Equation 1) is also influenced by many other factors, which in turn impact on the yield stress and hardness properties. These factors include processing conditions and loading direction, which is ultimately related to deformation modes in Mg alloys [56]. The value of $k$ is also affected by other boundary parameters [57] including temperature, but there is little work done on this.

**Conclusions**

The effects of RE alloying and cooling rate on microstructure features and mechanical properties of the ALa44, ALa413, ACe44 and ACe413 alloys were investigated. The results are summarised as follows:

- The cooling rate has a significant effect on the grain size, SDAS and intermetallic fraction, hence affecting the hardness and yield strength of the alloys. As expected, it was found that the hardness increases as the grain size and SDAS decreases, and intermetallic fraction increases at the higher cooling rate.
- The yield strength of the ACe44, ACe413 and ALa44 alloys behave in a manner consistent with the Hall-Petch relationship, in which a smaller grain size leads to higher hardness and yield strength. Whereas, ALa413 alloy behaved differently. The ALa413 alloy has the highest hardness, but the grain size is not the finest among all the investigated alloys. It was found that the hardness in this alloy is mainly dominated by the SDAS and intermetallic fraction given that this alloy has the lowest SDAS and the highest amount of intermetallic.
- Processing-microstructure-property relationships are developed for the investigated alloys. In particular,
  a. The relationship between dendrite growth time and SDAS using the commonly used empirical equation for SDAS.
  b. The relationship between the instantaneous cooling rate at liquidus and SDAS modified from the commonly used empirical equation for SDAS.
  c. Hall-Petch relationship between yield stress and grain size.
  d. Hall-Petch relationship between yield stress and SDAS.
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Using the relationships developed in this study, microstructure features and yield stress at a given cooling rate for the ACe44, ACe413, ALa44 and ALa413 alloys can be predicted.

Acknowledgement

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35. CompuTherm, Pandat software and PanMagnesium 2018 thermodynamic database, Madison, Editor.


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47. C. Wong et al. Experimental study of the solidification microstructure in the Mg-rich corner of Mg–Al–Ce system. in TMS Annual Meeting & Exhibition. 2018. Springer.


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Chapter 10

Conclusions and Recommendations
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10.1 Concluding remarks

Magnesium alloys have become increasingly attractive for use in transport applications due to their low density and high specific strength [1, 2]. This is especially beneficial for vehicle weight reductions and hence improved fuel efficiency. The commonly used magnesium alloys, such as AZ91, AM60 and AM50, tend to suffer from poor creep resistance, which limits their use in high-temperature applications. In comparison, AE alloys are found to have improved creep resistance properties [3, 4], however, the associated knowledge of the microstructure formation and how this affects properties is limited. This can hinder the design and optimisation of AE alloys for commercial applications. Therefore, this research was motivated by the increasing interest in magnesium alloys, especially AE alloys for use in elevated temperature applications in the automotive industry.

Although the AE series of alloys have been the subject of several previous studies, the majority of microstructural investigations have assumed that most RE elements in the mischmetal (i.e. Ce, La, Nd and Pr) behave similarly, producing the same set of intermetallic phases. An example of this is that the thermodynamic database for the Mg-Al-Ce and Mg-Al-La systems draws extensively on the same information. Furthermore, the prediction and control of microstructure formation under non-equilibrium solidification conditions remains a challenge in alloy design. This study set out to understand the microstructure development and solidification behaviour in AE alloys through investigating the effects of different ternary rare earth alloying additions (i.e. La or Ce) and cooling rates during the solidification process, using both experimental and thermodynamic calculation techniques. The key points of investigation in this thesis can be summarised as below.

- Identification of the intermetallic phases that are present in Mg-Al-Ce and Mg-Al-La alloys, in particular the identification of phases which have not been reported previously. In addition, whether or not the intermetallic phases are the same in Mg-Al-Ce and Mg-Al-La alloys has also been investigated. (Chapters 5, 7 and 8)
- Greater understanding of the solidification sequence of the alloys, including the formation of primary phases, and the determination of whether the alloys are hypo- or hyper-eutectic. The current experimental data is also compared and contrasted to that of the most recent thermodynamic predictions. (Chapters 4 and 6)
• Determination of the cooling rate effects on the microstructure and properties (hardness and yield strength) of Mg-Al-RE alloys. To develop generalised processing-microstructure-property relationships to predict mechanical properties of the alloys based on known cooling rates for the Mg-Al-RE alloys. (Chapter 9)

The results presented in Chapter 4 focus on the microstructure and phase diagram of Mg-Al-Ce alloys. This study was undertaken to understand the intermetallic phases that form in these alloys and to identify the key discrepancies between the experimental results and thermodynamic predictions to help improve the thermodynamic database for the Mg-Al-Ce system. Similar motivations also apply to the Mg-Al-La system. Hence, Chapters 5 and 6 are about the microstructure and thermodynamic analysis of Mg-Al-La alloys. These investigations into a series of Mg-Al-Ce and Mg-Al-La alloys revealed that the extent of intermetallic phase formation is not accurately predicted by thermodynamic calculations based on the published Mg alloy databases. The results from Chapters 4 to 6 therefore provided motivation for a comparative study of Mg-Al-Ce and Mg-Al-La alloys. In Chapters 7 and 8, the results from microstructure characterisation of the alloys with variations in Ce or La concentrations are presented. Lastly, the effects of cooling rates on microstructure features and properties of these alloys are presented in Chapter 9. The focus is to quantitatively characterise the relationship between processing – microstructure – properties of as-cast AE alloys. The results from this thesis can, therefore, provide a comprehensive understanding of the effects of individual RE alloying and cooling rate on the selection of intermetallic phases, microstructure features as well as solidification behaviour of Mg-Al-RE alloys.

This chapter summarises all key findings obtained from Chapters 4 to 9 of this thesis. The important contributions of this research and the scope for future work are also discussed in Sections 10.2 and 10.3, respectively.

10.1.1 Experimental study of the solidification microstructure in the Mg-rich corner of Mg–Al–Ce system (Chapter 4)

During the investigation of the solidification microstructure in Mg-Al-Ce alloys, shortcomings were identified within the published literature for the Mg-rich end of the Mg-Al-Ce phase diagram. Firstly, the intermetallic phase, Al₅Ce₂, was identified in the ACe310 and ACe412 alloys. This phase is isostructural with Al₅La₂, but has never been reported in the literature and it is currently not listed in the crystallography database. The refined lattice parameters of this phase ($a = 4.605 \text{ Å}$ and $c = 3.826 \text{ Å}$) are significantly different from the lattice parameters of
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Al₅La₂ ($a = 4.478 \text{ Å}$ and $c = 4.347 \text{ Å}$), which has been observed in Mg alloys previously. Secondly, the phases identified in these alloys contain some inconsistencies with the Scheil-Gulliver predictions from PanMagnesium 2017 thermodynamic database. One of the key discrepancies is in the position of the eutectic valley. In particular, this study showed that the ACe310 alloy is a hyper-eutectic alloy, whereas the thermodynamic predictions indicate it is a hypo-eutectic. Another discrepancy is that the observed intermetallic phases are not the same as the phases predicted by the Scheil-Gulliver equation. For example, the predictions indicate that the solidification process for these alloys terminates in the Al-RE region in the phase diagram, whereas the observed solidification path tends towards the Mg-RE region in the phase diagram as evidenced by the presence of the eutectic Mg₁₂Ce phase. These findings suggest that the thermodynamic database for the Mg-Al-Ce system needs to be further refined.

10.1.2 (Al,Mg)₃La: a new phase in the Mg-Al-La system (Chapter 5)

In this study, an investigation of the Mg-rich end of the Mg-Al-La system led to the discovery of a new ternary phase with the composition of (Al,Mg)₃La. Using high-resolution synchrotron X-ray powder diffraction and HAADF-STEM imaging on a Mg-4.5Al-6La alloy, the crystal structure has been determined. It was found to have an orthorhombic structure with a space group of $C222_1$ and lattice parameters of $a = 4.3365 \text{ Å}$, $b = 18.8674 \text{ Å}$ and $c = 4.4242 \text{ Å}$. The investigation has also confirmed that the (Al,Mg)₃La phase is distinctly different from the binary Al₅La phase (currently in the database), which is hexagonal with the space group $P6_3/mmc$.

10.1.3 Solidification path and microstructure evolution of Mg-3Al-14La alloy: implications for the Mg-rich corner of the Mg-Al-La phase diagram (Chapter 6)

This study was conducted to obtain a better understanding of the microstructure evolution in a Mg-3Al-14La alloy using a combination of ex-situ microstructural investigation and in-situ synchrotron radiography, which allows real-time observation of the solidification process. As a result, the solidification sequence of Mg-3Al-14La alloys is determined, which begins with the precipitation of a primary intermetallic phase, Al₅La₂, followed by a mono-variant eutectic reaction with products $\alpha$-Mg+Al₅La₂, then another mono-variant eutectic reaction producing $\alpha$-Mg+Mg₁₂La and lastly a ternary eutectic finalising with $\alpha$-Mg+Mg₁₂La+(Al,Mg)₃La. The solidification sequence is also found to be significantly different from the current Mg-Al-La thermodynamic description.
Firstly, it appears the Mg-3Al-14La alloy is a hyper-eutectic alloy rather than a hypo-eutectic alloy as currently described in the thermodynamic database. Secondly, the intermetallic phase is Al₅La₂ instead of Al₃La as predicted. It was also found that the primary Al₅La₂ is unlikely to be a potent nucleant for α-Mg grains, given that there is no favourable orientation relationship between the Al₅La₂ and α-Mg. Thirdly, the (Al,Mg)₃La phase identified in Chapter 5 is also present in this alloy. Because this newly identified phase is currently not in the thermodynamic database, comparisons between the experimental observations and thermodynamic predictions are complicated. This suggests that the thermodynamics of the Mg-Al-La system should be re-investigated.

**10.1.4 Revisiting the intermetallic phases in high-pressure die-cast Mg–4Al–4Ce and Mg–4Al–4La alloys (Chapter 7)**

Al₁₁RE₃ is commonly reported as the dominant phase in Mg-Al-RE based alloys, such as AE44. However, the newly identified (Al,Mg)₃La phase was found to be the predominant intermetallic in gravity-cast Mg-4.5Al-6La alloy (Chapter 5) and a minor eutectic phase in the Mg-3Al-14La alloy (Chapter 6). This initiated a re-examination of the Mg-4Al-4Ce (ACe44) and Mg-4Al-4La (ALa44) alloys. In this study, it has been confirmed that Al₁₁Ce₃ is the predominant phase in HPDC ACe44 alloys. However, (Al,Mg)₃La is the predominant phase in HPDC ALa44 alloys. The results from annealing experiments found that the Al₁₁Ce₃ and (Al,Mg)₃La are most likely to be the equilibrium phases in ACe44 and ALa44 alloys, respectively. Hence, the findings in this study confirm that the formation of intermetallic phases in Mg-Al-RE alloys is strongly influenced by the choice of individual RE alloying elements.

**10.1.5 A comparative study of the solidification microstructure in sand-cast Mg-Al-Ce and Mg-Al-La alloys (Chapter 8)**

Applying the knowledge gained from previous chapters, the effect of individual RE alloying is further investigated through a series of sand-cast Mg-Al-Ce and Mg-Al-La alloys. In the Mg-Al-Ce alloys, the primary Al₂Ce particles are found to be at the centre of the grains for Ce concentrations of 7 wt.% and above. This indicates that ACe44 is a hypo-eutectic alloy, whereas ACe47, ACe310 and ACe413 alloys are found to be hyper-eutectic, which is again inconsistent with thermodynamic predictions. On the other hand, the primary Al₅La₂ phase is only observed in Mg-Al-La alloys containing 11 wt.% La or more, such as ALa311 and ALa413. The Al₁₁Ce₃ eutectic phase is consistently found to be the predominant phase in the low Ce content alloys, such as ACe44 and ACe47. As the Ce content increases to 10 wt.% and 13 wt.% in ACe310 and ACe413 alloys, respectively, the Mg₁₂Ce eutectic is present and no
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evidence of Al$_{11}$Ce$_3$ is found in these alloys. In comparison, (Al,Mg)$_3$La and Al$_3$La$_2$ eutectic phases are extensively observed, regardless of the La concentration, in the Mg-Al-La alloys. However, as the La concentration continues to increase, the Mg$_{12}$La eutectic phase is also found in ALa37, ALa311 and ALa413. In addition, a small amount of MgLa is found in the ALa413 alloy. There is no evidence of either Al$_{11}$La$_3$ or Al$_2$La in these sand-cast Mg-Al-La alloys. Mg$_{17}$Al$_{12}$ is observed in ACe44 and ALa44 only, and not in higher RE-containing alloys. Again, the findings from this study have proven the intermetallic phase selection in the Mg-Al-RE alloys is strongly affected by the choice of individual RE alloying elements.

10.1.6 Influence of alloying elements and cooling rates on the microstructure features of Mg-Al-RE alloys (Chapter 9)

In this chapter, the effects of cooling rate on the solidification microstructure of Mg-Al-Ce and Mg-Al-La alloys were investigated using a series of wedge-cast alloys. One of the key findings in this study is that the secondary dendrite arms spacing (SDAS) and the grain size decreases with increases in the RE content of the alloys. Secondly, although various microstructure features affect the properties of the alloys, the yield strength of ACe44, ACe413 and ALa44 alloys are predominantly influenced by grain size as described using the Hall-Petch equation. On the other hand, the yield strength of ALa413 is predominantly influenced by SDAS and intermetallic phase fraction. Lastly, processing – microstructure – property relationships for the investigated alloys have been developed, which can be used to predict microstructure features and yield strength at a given cooling rate for these alloys. The following relationships have been developed,

- The relationship between freezing time and SDAS using the commonly used empirical equation for SDAS.
- The relationship between the pre-solidification cooling rate and SDAS modified from the commonly used empirical equation for SDAS.
- Hall-Petch relationship between yield stress and grain size.
- Hall-Petch relationship between yield stress and SDAS.

10.2 Contributions to knowledge

The interdependence between processing conditions and microstructure is important because it has a direct influence on the properties of the alloys. ICME tools, such as Pandat®, using the CALPHAD method, are powerful in alloy design and optimisation. However, these tools will only be useful if the predictions are accurate, which depends on a consistent thermodynamic
database. In this research, a comprehensive experimental study combined with thermodynamic calculations for high potential ternary Mg-Al-Ce and Mg-Al-La systems shows that the thermodynamic database was found to be inconsistent between the actual observations and predictions. First of all, the $\alpha$-Mg phase field in the Mg-rich corner of the phase diagram was found to be smaller than what is currently predicted in these systems. This influences the solidification sequence of phases during the cooling process, especially in castings. In Mg-Al-Ce system, it was found that the $\text{Al}_2\text{Ce}$ phase field is closer to the Mg-rich corner of the phase diagram (Figure 10.1(a)). Whereas, the $\text{Al}_5\text{La}_2$ phase was found to be a stable phase within a certain range of lanthanum concentrations, after which it becomes a metastable phase (this phase can be viewed in the liquidus projection by suppressing the thermally stable $\text{Al}_2\text{La}$ phase as shown in Figure 10.1(b) and (c)), and that the phase field of this phase is also closer to the Mg-rich corner in the Mg-Al-La system (Figure 10.1(c)). In addition, a new $(\text{Al, Mg})_3\text{La}$ phase was found to be a thermally stable phase when annealed at 500 °C for 100 hours in the ALa44 alloy. This phase is currently not in the thermodynamic database, which will have a great effect on the accuracy of thermodynamic predictions.
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Figure 10.1 Liquidus projection of Mg-rich corner of (a) Mg-Al-Ce system, (b) Mg-Al-La system without Al2La suppressed and (c) Mg-Al-La system with Al2La suppressed and generated by Pandat® using PanMagnesium 2018 [5], showing a hypothetical extension of Al2Ce and Al5La2 phase fields towards the Mg-rich corner, respectively. The α-Mg phase field is smaller than their current predictions. In addition, the (Al,Mg)3La phase is not in the thermodynamic database of Mg-Al-La system.
The outcomes of this research have also advanced the understanding of microstructure development and solidification behaviour of alloys in these systems with the effects of individual RE alloying elements. Previously Al\textsubscript{11}La\textsubscript{3} was commonly thought to be the dominant phase in the ALa\textsubscript{44} alloy given the similarity between the Mg-Al-Ce and Mg-Al-La systems. However, the discovery of a new phase in this research has proven that the dominant phase in the ALa\textsubscript{44} alloy is not the same as in ACe\textsubscript{44}. The ALa\textsubscript{44} alloy was found to contain a predominant (Al,Mg)\textsubscript{3}La stable phase, whereas ACe\textsubscript{44} contains a predominant Al\textsubscript{11}Ce\textsubscript{3} stable phase as commonly reported (Table 10.1). The microstructure evolution as the RE concentration increases in the two systems investigated is summarised in Figure 10.2.

**Table 10.1** Predominant and minor phases identified in HPDC ACe\textsubscript{44} and ALa\textsubscript{44} alloys.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Predominant phase</th>
<th>Minor phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACe\textsubscript{44}</td>
<td>Al\textsubscript{11}Ce\textsubscript{3}</td>
<td>Al\textsubscript{5}Ce\textsubscript{2}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al\textsubscript{5}Ce</td>
</tr>
<tr>
<td>ALa\textsubscript{44}</td>
<td>(Al,Mg)\textsubscript{3}La</td>
<td>Al\textsubscript{11}La\textsubscript{3}</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Al\textsubscript{5}La\textsubscript{2}</td>
</tr>
</tbody>
</table>
Chapter 10 Conclusions

Figure 10.2 Microstructure characterisation for sand-cast (a) Mg-Al-Ce alloys with Ce content and (b) Mg-Al-La alloys with La content range between 4 and 13 wt.%.

Lastly, generalised processing-microstructure-property relationships were developed for ACe44, ACe413, ALa44 and ALa413 alloys. These relationships can be used to predict microstructure features, in particular SDAS and grain size, with a known cooling rate. In addition, yield strength and hardness can also be predicted using the relationships developed based on the Hall-Petch equation. The list of relationships developed in this study is shown in Table 10.2.
Table 10.2 The relationships of processing-microstructure-properties for ACe44, ACe413, ALa44 and ALa413 alloys.

<table>
<thead>
<tr>
<th>Alloys</th>
<th>Processing-microstructure</th>
<th>Microstructure-properties</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_2 = M_l^n )</td>
<td>( \lambda_2 = M_2 \dot{T}^a )</td>
</tr>
<tr>
<td>ACe44</td>
<td>( \lambda_2 = 9.8 t^{0.39} )</td>
<td>( \lambda_2 = 203.2 \dot{T}^{0.73} )</td>
</tr>
<tr>
<td>ACe413</td>
<td>( \lambda_2 = 7.1 t^{0.39} )</td>
<td>( \lambda_2 = 238.8 \dot{T}^{0.91} )</td>
</tr>
<tr>
<td>ALa44</td>
<td>( \lambda_2 = 11.2 t^{0.57} )</td>
<td>( \lambda_2 = 328.9 \dot{T}^{0.79} )</td>
</tr>
<tr>
<td>ALa413</td>
<td>( \lambda_2 = 5.6 t^{0.35} )</td>
<td>( \lambda_2 = 196.8 \dot{T}^{0.85} )</td>
</tr>
</tbody>
</table>

In summary, the outcomes from the investigations in this research contribute to enhance the knowledge base of magnesium alloys, and hence it can be used to design alloys for specific applications, such as creep applications at elevated temperatures environment.

10.3 Suggestions for future work

Whilst this research offers some new insights into the solidification behaviour and microstructure development in complex ternary Mg-Al-RE alloys; there are several areas where more detailed testing and validation would be useful. Based on the findings of this research, the following recommendations are made for future investigations in the field of Mg-Al-RE alloys.

10.3.1 Thermodynamic database for Mg-Al-Ce and Mg-Al-La alloys

Although there has been some work published on the ternary phase diagram for Mg-Al-Ce system, and a relatively small amount of work has been published on the Mg-Al-La system, the findings in this thesis suggest that the thermodynamic databases for both of these systems should be remodelled and improved for greater accuracy of thermodynamic predictions. This can be carried out by incorporating the experimental findings presented in this thesis. In particular, the thermodynamic parameters of the recently identified \((Al,Mg)_3La\) phase should be determined and added into the CALPHAD thermodynamic databases.

Although the results from this study can contribute to improving the thermodynamic database for these systems, a series of alloys in different phase fields should be investigated to determine accurate invariant points and phase boundaries in the phase diagram.
10.3.2 Magnesium fraction in (Al,Mg)$_3$La phase
Although the chemical composition and crystal structure of the newly identified (Al,Mg)$_3$La phase have been determined in this thesis, it is difficult to quantify the Mg fraction precisely. Therefore, a further experimental study is needed to quantify the solubility limits for Al and Mg in this phase. Key experiments can be conducted by selecting a series of samples near to the composition of this new phase, to identify the effect of magnesium on the structure of this phase. In addition, the first-principles approach, such as density functional theory (DFT) for phase stability and solubility, can also be used to determine the solubility limits for Al and Mg in this phase.

10.3.3 Thermal stability of intermetallic phases
This thesis presents the intermetallic phases in the Mg-Al-RE alloys with Al$_{11}$Ce$_3$ and (Al,Mg)$_3$La being the thermally stable phases in the ACe44 and ALa44 alloys, respectively. The findings in this thesis also show that the Al$_{11}$La$_3$ phase is present in HPDC ALa44 but not in gravity-cast alloys. This indicates that the Al$_{11}$La$_3$ phase can be a metastable phase. Both stable and metastable phases influence the resultant microstructure during the solidification process. Hence, it is worth further investigations into the thermal stability of intermetallic phases in these alloys. Further investigation of phase thermal stability and the kinetics of the decomposition of intermetallic phases can be examined using a time series of aged samples.

10.3.4 Implement a heat transfer model to enhance the processing – microstructure relationships
In Chapter 9, the cooling rate obtained at the tip of the wedge-casting (thermocouple position 1) was determined using the extrapolation method, assuming the linear trend of the wedge cooling remains applicable. The assumption made in this study was employed to simplify a complex problem of solidification, which involves multi-phase changes. Therefore, a heat transfer model can be used to enhance the predictions and hence the processing – microstructure relationships. The phase-specific thermal properties could be used in the heat transfer model to further improve the accuracy of predictions. The alloying concentration and segregation during solidification can also be considered in a more sophisticated heat transfer model.

In addition, the processing-microstructure-property relationship developed in this study was based on four alloys in the Mg-Al-Ce and Mg-Al-La alloys. These relationships can be
improved if additional experimental data can be obtained. Hence, a thorough process model can be developed to relate the processing conditions to microstructure and properties.
10.4 References


Appendix A

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