Soldering in Magnesium High Pressure Die Casting and its Prevention by Surface Engineering

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DECLARATION

This thesis contains no material which has been accepted for the award of any other degree or diploma, except where due references is made in the text of the thesis. To the best of my knowledge, this thesis contains no material previously published or written by another person except where due reference is made in the text of the thesis.

Signed

Date
Abstract

Magnesium alloys are the lightest structural metallic materials and their importance in a range of industries has been rising in the last ten years. To the automotive and electronics industries, the most attractive properties of magnesium alloys are their light weight, strength to weight ratio, higher strength of thin/very thin section, high quality surface finish and precise dimension of cast components.

With the increased use of magnesium alloys especially in high pressure die casting, the phenomenon of soldering of magnesium alloys is attracting more attention. Soldering is the sticking of casting alloy to the die surface and leaving of drag marks on both the die and casting surface after part ejection. Soldering increases the rejection rate and the machine downtime, and serious soldering may damage the die which can cost hundreds of thousands, or even a million dollars to make. Because thin walled casting is one of the major advantages of magnesium high pressure die casting compared to other alloys, slight soldering can result in serious production problem.

This project is aimed at understanding the soldering problem in the magnesium high pressure die casting process and applying surface engineering approaches to reduce or even eliminate it.

A series of experiments was carried out to determine the factors that contribute to the soldering reaction which was followed by a number of surface engineering techniques to determine their effectiveness in reducing or eliminating it. Initially a preliminary study involving the dipping of H13 steel samples into AZ91D magnesium alloy was carried out. It was found that after short period of dipping, an intermetallic layer was formed on the sample surface. The intermetallic composes mainly of aluminium, iron and manganese, featuring two layered microstructure. Based on this finding, two groups of magnesium alloys were prepared to understand the role of alloying elements in the formation of intermetallic with H13 die steel. One group was alloyed with different aluminium contents (3%, 6% and 12%) in magnesium to understand the role of
aluminium. The second group was alloyed with different manganese contents in the Mg-3%Al alloy, to understand the role of manganese.

It was found that when the aluminium content was lower than 6%, no intermetallic layer was formed and this finding supports the literature data where 7% aluminium in magnesium is the critical value for the solubility of iron in the Mg-Al binary alloy. Nevertheless, when manganese was added to the magnesium alloy, even with 3% of aluminium, an intermetallic layer with a two-layered microstructure formed quickly. From this finding, it is concluded that manganese helps the formation of the Al-Fe-Mn intermetallic, which leads to soldering. The high pressure die casting trial using a specially designed die confirmed these findings.

Other than the Al-Fe-Mn intermetallic which formed as a result of reaction between the alloy and the die material, another two soldering modes were also found. They are the redox reaction between magnesium and the oxide layer on the die surface formed during die casting process, and the build-up of aluminium-manganese intermetallic particles on the die surface. Together with the intermetallic formation with the substrate, these three modes may occur on the different die locations in relation to the injection gate.

Following the dipping and high pressure die casting experiments several surface treatments were selected to reduce or eliminate the soldering problem. These included diffusion layers (nitride and oxide coatings), laser clad Fe/W, PVD coatings (TiN, CrN) and composite coating (PVD on the nitride coatings). The best performance was achieved with the duplex PVD coating of TiN/CrN with CrN next to the substrate. After 3 hours of dipping into both the Mg-12wt.%Al and Mg-3wt.%Al-0.52wt%Mn alloys, the coating’s surface looked intact, no reaction was observed by SEM and no phase change detected by X-ray diffraction analysis. TiN coating on grounded substrate performed similarly. This led to the finding that substrate’s surface roughness not only affects the intermetallic nucleation on the surface during high pressure die casting, but also affects the PVD coating’s performance. Composite coatings did not perform better than the same coatings without nitriding the substrate because of the lower decomposition temperature of the nitride products which degrade the bonding between the substrate and the coating.
This study has led to better understanding of the chemical reactions between the H13 die steel and magnesium alloys as well as the soldering mechanism in the magnesium high pressure die casting process. The application of coating technologies investigated can lead to the elimination of soldering in high pressure die casting of magnesium alloys.
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To be published papers

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Tang, C., Jahedi, M. and Brandt, M., Soldering in magnesium high pressure die casting.

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- Boland Forum, Monash University, 08-2003
- Simtech, Singapore, 03-2004.
Table of Contents

Abstract ................................................................................................................................. I

Acknowledgement ............................................................................................................... IV

List of Publications .............................................................................................................. V

Table of Contents ............................................................................................................... VI

Chapter 1  Introduction ........................................................................................................ 1

1.1 Die casting technology .............................................................................................. 1

1.2 Objectives of the study ............................................................................................ 3

1.3 Summary of chapters .............................................................................................. 4

Chapter 2  Literature Review .......................................................................................... 6

2.1 High pressure die casting (HPDC) ............................................................................. 6

2.2 Soldering in aluminium high pressure die casting .................................................... 9

2.3 Dipping test for the purpose of understanding the soldering mechanism .............. 13

2.4 Soldering in magnesium high pressure die casting ................................................... 15

2.4.1 General information about magnesium alloy ..................................................... 17

2.4.2 Morphology of AZ91D high pressure die casting magnesium alloy ............... 20

2.4.3 Al-Fe-Mn phases in Magnesium alloys ............................................................ 23

2.5 Surface engineering for prevention of soldering in High Pressure Die Casting of aluminium alloys ........................................................................................................... 26

2.5.1 Oxide coatings ..................................................................................................... 27

2.5.2 PVD, CVD and TRD coatings ............................................................................. 30

2.5.3 Comparison of coating methods ....................................................................... 32

2.5.4 Failure modes of the coatings .......................................................................... 36

2.6 Summary ..................................................................................................................... 37

Chapter 3  Experimental Methodology ............................................................................ 39

3.1 Understanding of the soldering mechanism in high pressure die casting of magnesium alloys ............................................................................................................. 39

VI
3.1.1 Dipping tests ................................................................. 40
3.1.2 Die casting ................................................................. 44
3.2 Coatings for soldering prevention ................................................. 47
  3.2.1 Oxide coating .............................................................. 47
  3.2.2 Nitriding ................................................................. 48
  3.2.3 Laser cladding of tungsten coating ................................... 50
  3.2.4 Physical vapor deposition .............................................. 52
3.3 Characterization and sample preparation ....................................... 54
  3.3.1 Polishing ................................................................. 55
  3.3.2 Removal of the cast alloy overlay ....................................... 55
3.4 Summary ......................................................................... 57

Chapter 4  Experimental Results ...................................................... 58
  4.1 Dipping tests .................................................................. 58
  4.2 AZ91D dipping tests .......................................................... 58
    4.2.1 Intermetallic layer morphology ....................................... 58
    4.2.2 Intermetallic phase identification ..................................... 61
  4.3 Mg-Al alloys dipping tests .................................................. 62
    4.3.1 Intermetallic layer morphology ....................................... 62
    4.3.2 Intermetallic phase identification ..................................... 67
  4.4 Mg-Al-Mn alloys dipping tests ............................................. 72
    4.4.1 Intermetallic layer morphology ....................................... 72
    4.4.2 Intermetallic phase identification ..................................... 76
  4.5 Summary of dipping experiments ........................................... 79
  4.6 Die casting trials .............................................................. 79
    4.6.1 Soldering morphology on the core pins .............................. 80
    4.6.2 Intermetallic compositions and phases identification ........... 82
  4.7 Summary ......................................................................... 88

Chapter 5  Performance of surface coatings in preventing soldering in magnesium alloys ................................................. 89
Chapter 1  Introduction

1.1 Die casting technology

There are many ways of shaping a metal in manufacturing industry to form a designed part, such as machining off unwanted material, joining two materials together, roll milling squeezing heated or cold material to simple shape and pressing the plate material to a certain shape. Since it was discovered that metal could also be melted, people have tried to form it into designed shapes by pouring the liquid metal into moulds whose shape it would retain during and after solidification. This process is called casting. If the mould is permanent it is called die casting[1]. Die casting has now developed into a very sophisticated manufacturing process that plays an important role in providing products for today’s high standard of living.

The earliest examples of die casting by pressure injection occurred in the mid-1800s with a patent awarded to Sturges in 1849 for the first manually operated machine for casting printing type [2,3]. By 1892, commercial applications included parts for phonographs and cash registers, and mass production of many types of parts began in the early 1900s. The die casting technique has evolved from the original low-pressure injection method to techniques including high-pressure die casting— at pressure exceeding 30MPa — squeeze casting and semi-solid die casting. High Pressure Die Casting (HPDC) is the most common and is classified into cold chamber and hot chamber high pressure die casting according to the injection method. The hot chamber high pressure die casting has the injection mechanism immersed in the molten alloy while in the cold chamber a ladling system (manual or automatic) is used to feed the chamber before the molten metal is plunge injected into the die cavity.

With the evolution of die casting technology, casting alloys have also evolved from tin and lead at the beginning to light metals, specifically aluminium and magnesium alloys since the 1930s. In the automotive industry, about 85-90% of aluminium used is produced by die casting.
Magnesium alloys are the lightest structural metallic materials and their importance in a range of industries has been rising in the last few years. To the automotive and electronics industries, the most attractive properties of magnesium alloys are their light weight, strength to weight ratio, higher strength of thin/very thin section, high quality surface finish and precise dimension of cast components [4-7].

The need for high volume, more accurate dimension, lower production cost, superior surface finishing and improved mechanical properties of castings is the driving force for the application of new technologies to die casting process. One of the areas that is receiving attention is the die surface. Hard coatings by means of Physical Vapour Deposition (PVD) [8-11], Chemical Vapour Deposition (CVD) [11,12], Thermal Reactive diffusion (TRD) [11], and laser cladding [13] have been investigated or adopted to die surface to improve the casting quality and extend the die life, Table 1-1. Bhushan [14] listed the requirements of a good coating material and its properties, Table 1-2.

Table 1-1. Some commonly used coatings and their application technique [14]

<table>
<thead>
<tr>
<th>Coatings</th>
<th>PVD</th>
<th>CrN, TiN, CrC, TiAlN, ZrN, VC, etc</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CVD</td>
<td>CrC, TiN, ZrN, VC, etc</td>
</tr>
<tr>
<td></td>
<td>TRD</td>
<td>VC, CrC, CrN, etc</td>
</tr>
</tbody>
</table>

Coating selection criteria includes [12]:

1) Adequate adhesion to substrate for longer life
2) Good mechanical properties
3) Corrosion and oxidation resistance
4) Shock resistance
5) High thermal conductivity
6) Dimensional stability
7) Thermal properties compatible with the substrate to minimise interface stress
8) Compatibility between the coating and substrate
9) Low surface wear
Table 1-2. Property requirement for an ideal coating [15]

<table>
<thead>
<tr>
<th>Property</th>
<th>Requirement</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hardness</td>
<td>High</td>
</tr>
<tr>
<td>Strength (Comp. and tens.)</td>
<td>High</td>
</tr>
<tr>
<td>Ductility</td>
<td>Moderate</td>
</tr>
<tr>
<td>Toughness</td>
<td>Moderate</td>
</tr>
<tr>
<td>Elastic Modulus</td>
<td>High</td>
</tr>
<tr>
<td>Thermal Conductivity</td>
<td>High</td>
</tr>
<tr>
<td>CTE</td>
<td>Low</td>
</tr>
<tr>
<td>Melting point*</td>
<td>High</td>
</tr>
<tr>
<td>Coef. Of Friction**</td>
<td>Low</td>
</tr>
<tr>
<td>Porosity</td>
<td>Low</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>Simple, High Symmetry</td>
</tr>
<tr>
<td>Chem. Compatibility***</td>
<td>Good</td>
</tr>
<tr>
<td>Composition</td>
<td>Close to Stoichiometry</td>
</tr>
</tbody>
</table>

*Relative to operating or developed service temperature

**Relative to opposing sliding surface

***Relative to counterface or environment

In addition to the above requirements, other factors should be considered when selecting coatings. These factors are as follow:

1) Commercial availability

2) Technical feasibility

3) Die material, size and shape.

It should be noted that it is almost impossible to develop a coating which can meet all the above listed criteria. These should be prioritised so that the coating performs optimally.

1.2 Objectives of the study

Molten aluminium is very aggressive, reacts with all metals and forms a series of intermetallic phases which are brittle and have undesirable properties. In high pressure
die casting, dies are mainly made from steel and the molten aluminium alloy reacts with it resulting in the formation of a hard, brittle intermetallic layer between the casting and the die. The formation of the intermetallic phase makes casting ejection difficult and leaves drag marks on the casting surface. This also causes damage to the die and any die repair leads to the down time of the machine and also reduces the accuracy of subsequent casting products. This phenomenon is called ‘SOLDERING’ in the die casting industry.

Soldering has also been reported by the magnesium die casting industry [16] but this is not as severe as in aluminium die casting. Unlike aluminium high pressure die casting in which soldering has received significant attention [17-25], little investigation has been done on soldering in high pressure die casting of magnesium alloys. It is a common belief that soldering in magnesium high pressure die casting seldom occurs because of low affinity between magnesium and iron. However, Al-Fe-Mn intermetallic phases were found in most magnesium alloys [26,27] and may play a critical role in soldering formation. As good surface quality and thin wall strength are two distinct advantages of magnesium high pressure die casting parts [5-7], slight soldering on the die surface may significantly degrade the casting surface quality.

The primary objective of this study is to understand the soldering mechanism in high pressure die casting of magnesium alloys and determine factors responsible for its formation. Roles of the major alloying elements, such as aluminium and manganese, as well as the die material, mainly iron, in the soldering reaction are examined.

The second objective of this study is to investigate a range of suitable coating technologies in order to reduce or eliminate soldering. The currently adopted method for the prevention of soldering is surface engineering which protects the die surface by means of PVD, CVD, TRD, laser cladding, shock hardening (peening) and oxide coating.

1.3 Summary of chapters

Chapter 1 outlines diecasting technology and introduces the concept of soldering. It then presents the disciplines of this study.
Chapter 2 reviews in detail the literature relating to soldering in high pressure diecasting of aluminium alloys. The metallurgical aspect of magnesium alloys in relation to the intermetallic reaction, mainly Al-Fe-Mn. Surface engineering technologies which reduce soldering in diecasting aluminium alloys are also reviewed in this chapter.

Chapter 3 introduces the methodology adopted to understand and reduce soldering in magnesium high pressure die casting. This includes initially finding the elements that are involved in the soldering reaction in preliminary dipping tests. From the preliminary results, aluminium and manganese in magnesium alloy were identified as the two major elements in the soldering layer and thus a series of detailed dipping tests was designed and carried out to understand their roles. Coatings and coating techniques adopted in this study for minimizing soldering are detailed in this chapter.

The results of dipping tests and high pressure die casting trials are presented in Chapter 4.

Chapter 5 presents the results of different surface technologies applied to minimize or eliminate soldering in magnesium alloys.

Chapter 6 discusses in detail the results of soldering experiments especially the roles of aluminium and manganese. Also included is the discussion on the effects of different surface engineering technologies on the prevention of soldering.

Chapter 7 presents concluding remarks on the soldering reaction in high pressure diecasting of magnesium alloys and surfacing technologies to eliminate it. It also includes recommendations for further work.
Chapter 2  Literature Review

Soldering is one of the main phenomena affecting die life and causing parts rejection due to surface defects and dimensional error. This review is focused on one common problem in high pressure die casting, the soldering and its prevention and elimination by applying surface treatment and coatings.

2.1 High pressure die casting (HPDC)

High Pressure Die-Casting (HPDC) is a widely used process in the manufacturing industry to produce near net shaped components [1,2]. Two basic types of die casting machines are hot chamber and cold chamber machine. The hot chamber die casting machine is used for smaller parts because of the lower lock force, and often traps air in the casting, especially because of the severe erosive and corrosive wear that occurs within the gooseneck, therefore it is not as popular as cold chamber machine. The cold chamber machine is mainly used for the casting of aluminium and magnesium alloys and can cast large parts with good mechanical properties, and is the focus of this research. The cold chamber die casting process consists of the following steps, as illustrated in Figure 2-1:

1. Ladling or pouring the molten alloy from the holding furnace into the space in the shot sleeve between the die and the plunger.

![Figure 2-1. Stages of High Pressure Die Casting [17]](image)
2. Injecting the melt into a die cavity through a thin slit or gate at high speed (30-100 m/s, sometimes as high as 200 m/s) by the forward movement of the plunger.

3. Holding the die under high pressure (40-120 MPa) and letting the melt solidify at a high cooling rate, 100-1000 °C/s, which is helpful for the formation of fine grained casting. Holding the die at high pressure not only reduces the porosity produced during filling and solidification but also reduces the contact thermal conducting resistance between the die and the alloy thus increasing the productivity and surface quality.

4. Ejection of the casting to separate the casting from the die.

5. Die cooling and lubrication with water and lubricant mixture. Die cooling during die holding helps reduce the solidification time. Die spraying also helps to cool the die, but more importantly spraying of water based lubricant deposits a thin layer of lubrication material on the die surface which prevents soldering and makes the casting ejection easier.

The load conditions during each stage make great demands on the quality of the die material and therefore the type of die steel is critical to the quality of castings and continuous operation of the die [28,29]. H13 is a hot-work tool steel which possesses good strength and hardness at high temperature and is widely used in manufacturing of dies. Under the high pressure die casting manufacturing circumstances, mechanical, physical and chemical reaction can occur with the die and cause the die failure. Biernat and Goodling [30] schematically showed the main die failure modes, Figure 2-2. They are termed as:

1. Heat checking due to the repeated heating by the melt and cooling by the coolant, resulting in severe thermal stress which induces cracking;

2. Erosive and abrasive wear due to the impingement of the melt which may contain particles precipitated before injection under high pressure. Some dies are very complicated in shape and are more prone to the wear phenomenon.
Wearing leads to, in the short term, the damage of the thin protective layer formed during die spray and, in the long term, the changing of the die dimensions;

3. Soldering due to the sticking of the casting material to the die surface after the casting ejection. Soldering is separated into two different types:

1) Sticking of metal because of the mechanical attachment, which might be eliminated by the following shot(s).

2) Sticking of metal because of the chemical bonding resulting in the formation of the intermetallic compound (IMC, alloying of the melt with the tool steel).

Soldering can hinder the ejection of the casting from the die and cause drag marks on its surface. These marks are responsible for casting rejection as they affect the casting surface quality especially when its walls are thin.

Figure 2-2. Typical failure modes of the die casting dies [30]
2.2 Soldering in aluminium high pressure die casting

Soldering in the aluminium high pressure die casting process has been investigated extensively by a number of researchers [8,17-25,31-35]. Two soldering mechanisms have been proposed.

The first one suggests that soldering is a series of steps involving erosive wear, corrosive wear, dissolution of die materials, and development of intermetallic phases [20]. Generally, soldering starts at the spot facing the injection gate. Under high melt injection velocity and high temperature, the protective thin coating (oxide coating) on the die surface may be worn off and allow direct contact between the die steel and cast aluminium alloy[20].

In aluminium die casting the alloy melt temperature, which is held at 680-690°C, drops to or is lower than the eutectic temperature in the shot sleeve before being injected into the die cavity. Only near the pouring ladle is the melt temperature slightly higher than 570°C [17]. This lowering of temperature causes some solid particle precipitation which accelerates the erosive wear and the damage of the thin protective coating (oxide coating) on the die surface. It is also noticed that the die colour may change because of the erosion. The contour or shape of the specially located core pin changed with heavy wash-out occurring. The corrosive wear and inter-diffusion is easily started when the protective coating is broken and removed leading to the formation of the soldering layers. Corrosive wear reaction is defined as dissolution of steel in the melt and the formation of intermetallic layer [33]. Iron dissolves into the alloy melt and Al and Si diffuse into the substrate to produce Al-Si-Fe and Al-Fe-Cu alloys or intermetallic compounds (IMC) [33,36,37]. Although they all contribute to the soldering process, only the intermetallic layer which is the result of chemical reactions remains on the die surface.

The main factors affecting the diffusion of aluminium, iron, silicon and other elements between the die steel and the casting alloy are the concentration gradients of the diffusing species, their atomic nature and temperature. The distribution of the elements in the soldering layer for the H13-A390 system is shown in Figure 2-3a. The major soldering
elements, Al, Si and Fe in the soldering layer have a high concentration gradient from the cast alloy to the die steel substrate.

Figure 2-3. Intermetallic structure. a) Element distribution profile in a die casting soldering layer, after [20] and b) intermetallic layer formed in dip test [39]
According to the Hume-Rothery Rules [38], the main factors which affect the formation of primary substitutional solid solution are:

1. An atomic radius difference less than 15%
2. Similar electronegativity and
3. Same crystal structure.

The radii difference between aluminium and iron is less than 15% and they also have similar electronegativity. These two factors mean that the formation of Al and Fe substitutional solid solution is favoured. Only their crystal structure reduces their solubility.

According to Chu et al. [20] the soldering formation is an indication of corrosive phenomenon and its nucleation is due to the affinity of aluminium for iron and silicon. With the formation of an intermetallic layer, the soldering grows and spreads quickly. This is understood as follow: after the intermetallic layer is nucleated, further growth will use this existing intermetallic layer as a substrate instead of the die steel, therefore the growth needs much lower surface activation energy. The intermetallic layer is usually hard and brittle with poor heat transfer characteristics [90]. Therefore, as soon as the intermetallic layer is formed it is difficult to be removed in the die casting process. It makes the die surface rough and more cast alloy can stick to it. With poor thermal conductivity, the soldered area is kept under higher temperature for a longer time than the area without intermetallic on it. This area is referred to as a hot spot and intermetallic in this area will grow and spread in time. These spots remain hotter and spread, as a result, the whole area becomes covered by the intermetallic layer.

The typical intermetallic structure from the dipping test of Al-11Si-3Cu alloy consists of 3 layers, Figure 2-3b [39]. The inner, compact η-Fe2Al5 layer, and the mixture of Al, Si, αFe–Fe2SiAl8, and αbcc(FeAlSiCrMnCu) composite layer. Most phases appeared in the inner layer and the composite layer the outer compact layer.
The growth and dissolution of the Fe$_x$Al$_y$ intermetallic at the interface between the die surface and casting aluminium alloy is described by Gopal [33] to occur in four stages:

1. Diffusion of the iron and the aluminium atoms in the opposite directions, towards the solid-liquid interface resulting in the formation of Fe$_x$Al$_y$ intermetallic layer.

2. Iron atoms from the substrate diffuse across the Fe$_x$Al$_y$ layer towards the Fe$_x$Al$_y$/Al interface and react with the aluminium atoms. This results in the movement of the intermetallic layer towards the aluminium alloy side or the growth of the intermetallic layer.

3. Similarly, the aluminium atoms diffuse across the Fe/Fe$_x$Al$_y$ interface to react with the Fe atoms. This results in the movement of the intermetallic layer towards the substrate side or the growth of the intermetallic layer.

4. Simultaneously, as the Fe$_x$Al$_y$ layer dissolves in the liquid metal, the Fe$_x$Al$_y$/Al interface will also move towards the substrate side. This stage accounts for the weight loss or recession in the dimensions of the core pin, insert and die substrate.

However, Chen and Jahedi [31] theoretically analysed liquid impingement erosion, solid particle erosion and cavitation erosion and conducted diecasting trials with a specially designed die in which the cast core pin was located facing the die filling gate. They concluded that die erosion is unlikely to occur in a short time (50-94 casting shots) or at least die erosion won’t occur before soldering occurs. This finding [31] suggested that the soldering mechanism is more complex and needs to be revised.

Based on further experiments, Chen [31] proposed the second soldering mechanism in which soldering is caused by corrosive wear due to the strong affinity of aluminium for iron in the die steel [17,39,40]. During the die filling and solidification processes, the casting alloy reacts with the die steel and forms complex intermetallic compounds at or
below the liquidus temperature of the cast alloy. Soldering starts with localised intermetallic formation accompanied by build-up of solidified cast alloy on the core pin surface [17,37]. As soon as the build-up layer is formed, it can not be fully remelted and removed because of the cast alloy’s low temperature. This implies that the development of the intermetallic/soldering layer mainly occurs in solid state. Chen [17] also points out that of all the factors that may influence the soldering process, cast alloy temperature and solidification time are the most important. From this point of view, the soldering reaction is similar to that of hot-dipping aluminising [41] although measurements of the melt temperature in the shot sleeve showed that the temperature in die cavity is very close to the liquidus temperature while in the hot-dipping process the temperature is about 100°C above the liquidus temperature [17].

2.3 Dipping test for the purpose of understanding the soldering mechanism

Dipping or immersion test involves a specific solid metal to be immersed into another metal’s melt at certain temperature for a certain period of time in order for reactions between the two different metals to occur. These reactions form an intermetallic layer on the solid metal surface that may act as either chemical or physical modification layer. The intermetallic layer normally has a multiple layer structure with different phases present in each layer. Aluminizing of iron to obtain an effective coating is one of the most popularly applied and studied processes. For the purpose of understanding the soldering mechanism in high pressure die casting and identifying phases at the die steel and the casting alloy interface, many researchers adopted this process with different aluminium alloys and sometimes with different die steel [20,21,23,29,39,41-44].

Dipping test can be divided into dynamic dipping and static dipping. The dynamic dipping test is usually carried out with a relative movement between the sample and the melt [44,45]. The static dipping, on the other hand, is carried out without this relative movement. Samples are simply immersed into the melt and held for a certain period of time. The difference in metallurgy between the two methods is mainly observed with the dissolution rate of the substrate [12]. The side of the immersed sample facing the
movement against the molten aluminium alloy encounters more material loss but there is no evidence that different intermetallic was produced because of the sample movement.

Among all the Fe-Al phases, FeAl₃ is the most thermodynamically stable but its formation only takes place under proper composition and cooling rate [46]. In most cases, the first intermetallic produced in Fe-Al, Fe-Al-Zn and Fe-Al-Si systems is the orthorhombic η-Fe₂Al₅ [39,42,47,48], which has a low thermodynamic stability. Even at very low Al-content (0.05 wt.%), Fe₂Al₅ is the most favorable phase formed [47]. This layer may act as a barrier coating to the formation of Al-Zn in Al-containing Zn bath [47]. There are several reasons for the preferential formation of Fe₂Al₅. One, according to Gusak’s model [49] is that if diffusion is much faster in a phase than in the other concurrent ones, this phase grows preferentially. In Fe₂Al₅ the inter-diffusion is 10-100 times faster than in FeAl₃ at 1000°C so it forms first [47]. Second, as explained by Heumann [50], there are specific defects in the crystal lattice of Fe₂Al₅ favoring influx of aluminium atoms to the growth front of the crystal.

Silicon is another important element which affects the intermetallic phase formation but there are some doubts regarding its effects in the reaction of Fe-Al-Si system[42,43,51,52]. Some authors found that the silicon atoms occupy the structural vacancies in the η-Fe₂Al₅ phase resulting in reduced diffusion possibilities for aluminium atoms [51,52]. Eggeler’s experiment confirmed this result [42]. Lainer and Kurakin (as cited in [42]) also found that in silicon containing aluminium alloy melts, intermetallic phases (FeₓAlᵧSi₂) are obtained but grow more slowly than the η-Fe₂Al₅ phase. In both cases, the presence of Si results in a slower solid state growth because Si inhibits the growth rate of intermetallic by either reducing the Fe dissolution or increasing the diffusion of Fe in intermetallic to the melt leading to the dissolving of the intermetallic phase [43]. When Fe is immersed in pure aluminium melt, 65wt.% of iron was used to build the η-Fe₂Al₅ layer and 35wt.% of it was dissolved into the aluminium bath. In the case of Al-8Si melt, 30wt.% of the iron was used to build the intermetallic compound and 70wt.% of it was dissolved into the Al-Si bath.
There are also some opposite opinions regarding the effect of Si. Silicon content in Al-alloy melts also affects the intermetallic phases. Winkelman [21] reviewed literature and summarized that with different Si contents, although the inner layer is still Fe$_2$Al$_5$, the phase in the outer layer (layer close to the Al-alloy) is different, as shown in Table 2-1.

Table 2-1. Si contents in the melt and intermetallic phases [21]

<table>
<thead>
<tr>
<th>Silicon content</th>
<th>Inner layer</th>
<th>Outer layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2%</td>
<td>Fe$_2$Al$_5$</td>
<td>FeAl$_3$</td>
</tr>
<tr>
<td>2-10%</td>
<td>Fe$_2$Al$_5$</td>
<td>FeAl$_3$ or α(Fe-Al-Si)</td>
</tr>
<tr>
<td>&gt;11%</td>
<td>Fe$_2$Al$_5$</td>
<td>α(Fe-Al-Si)</td>
</tr>
</tbody>
</table>

Aluminizing conditions (temperature and immersion time) affect the intermetallic formation, as well as its thickness and phases. El-Mahallawy [43] found that during Al-Si reaction with Fe, temperature and dipping time only affect the thickness of the intermetallic layer, not the phases [43]. Nevertheless, Yan and Fan [45] found that dipping time doesn’t have much effect on the thickness of inner Fe$_2$Al$_5$ layer and with long time immersion (9 hours), a thick, compact new phase (Fe, Cr, Mn)Al$_2$ was formed next to the FeAl$_3$.

There are some other factors that may also affect the aluminizing process, like melt and substrate compositions, (for example Fe content in Al-alloy melts and substrate material [21], surface conditions, such as roughness, hardness and treatment (oxidation) [23], however aluminium and iron intermetallic formation is the most important step leading to soldering in high pressure die casting.

2.4 Soldering in magnesium high pressure die casting

Compared with the soldering of aluminium alloys in high pressure die casting, the soldering of magnesium alloys has not received much attention. The general impression is that because magnesium doesn’t have the same affinity for iron as aluminium soldering will not occur. There are a number of reasons for this. As shown in Figure 2-4 [38]
elements within the oval have higher than 5% solubility in magnesium. As iron has a very different atomic radii (>15%) and electro-negativity compared with magnesium it therefore has a very low solubility.

The quantity and distribution of an intermetallic phase can have a marked effect on the properties of the alloys. Typically, for magnesium die casting alloy AZ91D, the intermetallic phase $\beta$-Mg$_{17}$Al$_{12}$ on the cast’s surface greatly increases its mechanical and corrosion properties [5,6,53,54], but on the contrary a very small amount of Fe (~0.005%) in the alloy will greatly reduce the mechanical and corrosion property of the casting [55-57]. In commercial high pressure die casting of magnesium alloys the intermetallic mainly contains aluminium, manganese and iron in binary or ternary forms [57-60]. Thus the intermetallic formation in magnesium alloys may occur when molten magnesium alloy is in contact with the die surface during the high pressure die casting process. This can then lead to soldering. Although there is no published data relating to the magnesium soldering in high pressure die casting, Chen [16] reported that soldering
occurred during high pressure die casting of AZ91D and that intermetallic particles in the soldering layer are aluminium, manganese and iron. Murray [61] noticed that soldering is more likely to occur when die casting magnesium alloys (AM60 for example) with higher manganese content. All these observations demonstrate that soldering in high pressure die casting magnesium alloys was occurring as a result of intermetallic formation, however the exact mechanisms were not fully understood.

2.4.1 General information about magnesium alloy

Magnesium is rarely used for engineering applications in its pure state because of its poor physical and chemical properties though it is the eighth richest element in nature. Its crystal structure is hexagonal with c=5.199 kX and a=3.202 kX, as shown in Figure 2-5. Its basal plane being close packed and the axial ratio only slightly greater than the theoretical value for the incompressible spheres [62].

![Diagram of magnesium crystal structure](image)

Figure 2-5. Principal planes and direction in the magnesium unit [66] cited in [67]
Commercial magnesium alloys are usually alloyed with aluminium, zinc, lithium, cerium, zirconium, and sometimes with rare earth metals. Addition of these elements result in different alloy properties [63,64]:

1. Aluminium: Addition of aluminium to magnesium alloy is good for both room temperature strength and fluidity. Mg alloy with 10% aluminium has a 300% higher fluidic ability compared with that with only 2% aluminium. The increase of Al content increases magnesium alloy’s strength at room temperature, however, it also results in a decrease of its toughness through the formation of a brittle intermetallic phase, which causes the elevated temperature strength to decrease. Two major phases exist in the Mg-Al system when the aluminium content is higher than 2wt.%, α-Mg grains and β-Mg_{17}Al_{12}, the latter is sometimes referred to as Mg_{4}Al_{3} [65]. The Mg-Al binary phase diagram, Figure 2-6, suggests that cooling the molten metal below 600°C will cause Mg (solid solution) crystals to begin to form within liquid magnesium alloy. The maximum solubility of aluminium in magnesium is 11.8 at.% at the eutectic temperature of 437°C. Further lowering the temperature may result in the precipitation of β-Mg_{17}Al_{12}. This phase has an α-Mn structure and the ideal crystal structure with 58.6 at.% Mg. At 450°C, its maximum composition ranges from ≈45 to 60 at.% Mg, as shown in Figure 2-6.
2. Zinc: The zinc content promotes the fluidity and room temperature strength, however, an increase in the brittleness of the component can result as the zinc content increases. If the zinc content is higher than 2wt.% the component tends to hot crack.

3. Manganese: Manganese is found in all common Mg-alloys. It is considered to be important for the homogeneity and results in the better corrosion property of the alloy by lowering the Fe content by forming the Al-Mn-Fe intermetallic phase. However, it has the disadvantage of an increased segregation capability when its content is above 0.4%. Subsequently, the element can be found in high concentration in the bottom sludge.

4. Silicon: Although it can increase the creep strength of the alloy at elevated temperature by forming SiMg₂ phase, silicon is regarded as unwanted. Besides being found as inclusions in the component, silicon is also present in the bottom sludge.
Inclusions in the component can result in machining problems. Furthermore, it is a corrosion promoting element.

5. Beryllium: Beryllium is added to minimize the oxidation of the molten magnesium alloy

6. Rare Earth Elements: These elements, such as neodymium, are alloyed to improve creep strength. They also contribute to broaden impurity tolerance limits required for high purity corrosion performance of the AE42 system.

7. Iron/copper/Nickel: These elements are considered absolutely undesirable in magnesium alloys. They lower the corrosion resistance considerably.

For the above reasons, the most commonly used magnesium alloy in high pressure die casting is high purity AZ91D [63,64]. This alloy shows excellent castability and good strength combined with fair ductility. It also provides corrosion properties comparable to those of Al die casting alloys, as verified by numerous examples where parts are used without surface protection [63]. This is why it is always considered as the first choice alloy unless it is ruled out by specific property requirement. Other alloys such as AM60, AM50 and AS41 are also used as die casting alloys because of their good casting properties.

2.4.2 Morphology of AZ91D high pressure die casting magnesium alloy

AZ91D, designated according to its alloying element composition of A-8.3-9.7wt.%Al, Z-0.35-1.0wt.%Zn and high purity D, is the most common magnesium die casting alloy. Sequeira et al. [5] studied the microstructure of a series of casting samples with different thickness, and found that the castings show a distinct fine surface layer and a coarse grained interior. The surface layer extends to a thickness of up to 0.25 mm. Scanning electron microscope (SEM) images showed that there are two major phases in the castings, the super saturated solid Al solution in α-Mg grains (sizes ranging from 1-10 micron at the surface to 15-20 micron in the center) [5,62] which is separated by another
phase, the inter-granular β-Mg\textsubscript{17}Al\textsubscript{12} intermetallic phase. From the center of the casting to the surface, the fraction of β-Mg\textsubscript{17}Al\textsubscript{12} increases and the micro hardness is 15~20HV higher than that in the center. Electron microprobe analysis shows that both Al and Zn content increased at the surface whereas those in the large dendrite grains have lower contents than the average. Table 2-2 shows the chemical analysis of the sample used in the experiment.

The surface layer, according to Sequeira et al.[5], is very important to the mechanical properties of the die castings, especially for the thin walled components. With removal of 0.125mm from both surfaces of the 1mm thick flat samples, the yield stress decreased from 186MPa to 160MPa. All those surface effects were thought to be due to the higher β-Mg\textsubscript{17}Al\textsubscript{12} content in the surface layer.

Table 2-2. Chemical analysis in the bulk and the skin, and the electron microprobe analysis of large grains/dendrites in AZ91D high pressure die castings [5]

<table>
<thead>
<tr>
<th>Die cast specimen</th>
<th>ICP-AES chemical analysis (wt%)</th>
<th>Electron microprobe analysis of large grain/dendrite (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Bulk analysis</td>
<td>Skin analysis</td>
</tr>
<tr>
<td></td>
<td>Al</td>
<td>Zn</td>
</tr>
<tr>
<td>1mm flat</td>
<td>7.96</td>
<td>0.73</td>
</tr>
<tr>
<td>2mm flat</td>
<td>8.27</td>
<td>0.74</td>
</tr>
<tr>
<td>6mm flat</td>
<td>8.4</td>
<td>0.73</td>
</tr>
<tr>
<td>6.4 round</td>
<td>8.55</td>
<td>0.69</td>
</tr>
</tbody>
</table>

*Values in brackets indicate standard deviation of one sigma [5]

Further study by Unigovski and Gutman [6] using Auger electron spectroscopy (AES) gave more details on the composition of Al in the surface layer of both as cast and heat-treated AZ91D specimens. With an increase of sputter time up to 10-15min (10nm/min) the atomic aluminium contents reached 32% and 44% for the as cast and heat-treated specimens respectively. With decreasing distance to the surface, EDX analysis also showed that the aluminium content in α-Mg grains increased significantly. From 200 µm to 20 µm near the surface, the aluminium content increased from 5±1 to 12±5 at.%. In the
immediate vicinity of the casting surface this value reached $18\pm4$ at.%. The higher Al-content in the surface layer is thought to be due to its diffusion and temperature gradient during solidification. Aging sample at $200^\circ$C leads to a greater completeness of diffusion that results in the observed increase of atomic aluminium content in the specimens.

Unigovski [6] also found that with increased casting temperature from $630^\circ$C to $740^\circ$C, the contents of $\beta$-$\text{Mg}_17\text{Al}_{12}$ decreased at the cast surface from 50% to 45%, and the thickness of the $\beta$-$\text{Mg}_17\text{Al}_{12}$ layer also decreased from $13\mu$m to $2\mu$m.

There are no papers explaining the reasons for this phenomenon, but the ‘Alumina Gradient Effect’ may indirectly answer this question [54]. In the die casting microstructure of the magnesium composites containing alumina, a lower volume fraction was found at the casting surface than in the center region which is caused by velocity and shearing rate. In high pressure die casting of magnesium, the casting alloy is normally in the semi-solid state when entering the die cavity, containing quite a high fraction of solidified $\alpha$-magnesium [54]. As magnesium alloy in this state is injected into the die cavity via the gate and flows through the gauge length (after hitting the wall), a shear layer may be expected to develop due to velocity gradients across the section of the semi-solid slurry [54]. It has been shown that particles suspended in this flow can experience two transverse forces due to the presence of velocity gradient in the fluid caused by a shear layer near the wall [54]: the magnus force and the slip-shear force. In well mixed suspensions of spheres in viscous liquids rotating between rotating concentric cylinders, particles have been shown to migrate from the high shear rate region near the inner rotating cylinder to the low shear rate region of the outer wall. Thus, in the semisolid state of magnesium alloy, the $\alpha$-Mg would migrate to the region of highest velocity and lowest shear rate, the center of the casting. Thus it is possible that this action may leave the aluminium richer melt towards the outer surface of the casting.

From the above literature, it is clear that at the surface of the casting the aluminium content is higher than that in the bulk state. In contact with other materials, such as shot sleeve, goose neck and die, during the solidification of the Mg alloys, chemical reaction might occur between casting alloy elements and steel elements. For most die casting
magnesium alloys, manganese is an important addition. The Al-Mg-Mn system might also be a major reaction system. So the next part of this review is focused on these two systems.

2.4.3 **Al-Fe-Mn phases in Magnesium alloys**

2.4.3.1 Phases in magnesium alloys containing Mn and Fe

Simensen [60] observed three Al-Mn equilibrium phases in magnesium alloys containing 0.8 to 10wt.% aluminium and saturated with Mn, the $\beta$-Mn(Al), $\eta$-Al$_8$Mn$_5$ and Al$_{11}$Mn$_4$.

$\beta$-Mn(Al)(solid solution of aluminium in $\beta$-Mn)-appears when the aluminium content ranges from 0.8-4.0wt.%. Cubic lattice parameters are a function of the aluminium content. With increasing aluminium content in this range, the lattice parameter increased from 0.641 to 0.642nm. Another crystal of it structure is tetragonal.

$\eta$-Al$_8$Mn$_5$-appears when the aluminium content ranges from 3.8 to 9.8wt.%. It has hexagonal or rhombohedral structure with lattice parameters $a=1.27$nm, $c=1.59$nm. Aluminium in this phase increased from 53 to 59 at.% on increasing the aluminium content in the melt from 3.8 to 9.8wt.%.

Al$_{11}$Mn$_4$-appears in Mg-10wt.%Al-0.2wt.%Mn alloy at 670°C. It contains 73at.% Al, 26at.% Mn and 0.6at.%Fe and has a triclinic structure. All these were also observed by Mukhina [57].

Al$_6$Mn, Al$_2$Mn, AlMn as well as the above mentioned three equilibrium phases were found in ordinary castings. The AlMn phase was described as a disc-shaped particle and had a hexagonal structure [57]. Compared with Lashko's result [59] in which AlMn was identified as tetragonal, Mukhina [57] suggested that AlMn might be a metastable phase.

According to Mukhina [57], in a Mg-Al-Fe system, with aluminium content higher than 0.42wt.%, the independent FeAl phase starts to form. When the aluminium content reaches 1.8wt.%, the amount of FeAl phase increased and there was a heterogeneity in
the solid solution with the formation of aluminium-enriched zones. When aluminium content increased to 4.9wt.%, a small amount of Fe₂Al₅ was formed in addition to the FeAl. With 9.3wt.% of aluminium, the Fe₂Al₅ was the dominant phase present. Both FeAl and Fe₂Al₅ can act as effective cathodes which may reduce the corrosion resistance of magnesium alloys[57].

Lashko et al. [59] studied phases present in the commercial magnesium alloys, including Mg₁₇Al₁₂, and found that iron and manganese do not dissolve in this phase but form independent phases not including magnesium. They also found that in the binary alloy the intermediate phase, Fe₂Al₅ was formed, not the aluminium-rich FeAl₃. This is thought to be due to the defective structure of Fe₂Al₅. In addition to this, they also found that a considerable amount of manganese could be dissolved into the FeAl phase, its lattice parameter increasing from 2.89Å to 2.92Å. When the aluminium content in magnesium alloys is higher than 5wt.%, the Fe₂Al₅ formed. A Mn dissolved phase (Fe, Mn)₂Al₅ was identified with composition 11.55at.%Mn, 15.75at.%Fe and 72.7at.%Al from the Mg-8%Al-0.05%Mn-0.04%Fe alloy. It was observed that in Mg-Al-Mn system, when the manganese content exceeds 0.1%, iron does not form an independent compound but is dissolved in the Mn-Al system, replacing the manganese atoms [59].

2.4.3.2 Solubility of Fe and Mn in magnesium alloys

The iron content in magnesium alloys is very important because it is a controlling factor for the corrosion property of the alloys. Baker et. al. [27] published their results on the solubility of iron in magnesium alloys in the presence of aluminium and manganese in the alloy and found that with the aluminium contents in the range 2-7 wt.%, the iron solubility is little affected by aluminium (at 650°C, this solubility is around 0.005%), but is greatly affected by temperature. When the temperature reaches 900°C, this value is 0.07%. This result is verified by Simensen et al. [60]. In his research, 7 wt.%Al was a turning point before which iron solubility was not changed with aluminium. When the aluminium content was higher than 7 wt.%, this value increased abruptly. On the other hand, the solubility of manganese decreased readily with temperature, and with increasing aluminium content, as shown in Figure 2-7. Philips [69] noticed that with the
presence of manganese in the aluminium rich magnesium alloys, the solid iron solubility is negligible while the presence of iron decreases the content of magnesium in solid solution. The x-ray diffraction and chemical analysis found that the crystal structure and chemical composition of FeAl₃ in the ternary eutectic Al-FeAl₃-Mg₂Al₃ section and the pure FeAl₃ were the same which indicates that magnesium can not be dissolved in the FeAl₃ [70].

The effect of Mn on suppressing Fe in Mg-alloys may be thought of as being due to the high Mn content producing more Al-Mn phases into which Fe can be dissolved therefore lowering the Fe content. Adding an excessive amount of manganese can result in an alloy with a very low iron content, as was observed by Bronfin et al. [26], Figure 2-8.

Figure 2-7. Fe and Mn solubility as a function of Al content in magnesium alloy. After [60]
2.5 Surface engineering for prevention of soldering in High Pressure Die Casting of aluminium alloys

The complex process features occurring in High Pressure Die Casting are the key factors in understanding and prevention soldering. As was mentioned in Section 2.2, the die in high pressure die casting encounters three destructive types of wear\[17\][20][33,36,37]:

1. Erosive wear caused by the high injection rate (up to 200m/s). Under this high injection speed, the alloy melt, which contains solidified particles of intermetallic containing Al, Fe, Mn and Si, etc may cause severe erosive wear. Complex stresses exist because of high impingement pressure (up to 80MPa) and thermal heating and cooling, especially at the die surface.

2. Corrosive wear: High temperature (>600°C) in the casting environment means that the die surface in contact with the alloy melt encounters diffusion corrosion, or corrosion wear.

3. Thermal wear: Alternate cooling and heating in the process may cause heat checking, or thermal wear.
Soldering in high pressure die casting can be attributed to the combined action of the above three wear mechanisms with metallurgical factors. Erosive damage and heating of the die surface during the direct contact of the die and the alloy melt leads to soldering.

To prevent soldering in high pressure die casting, various methods have been tried [18, 23, 25, 35, 36, 71, 72]. The most common and simple method has been to apply a lubricant spray onto the die surface between each casting cycle. The spray of lubricant at the start of early shots forms a thin film on the surface of the die which acts as a barrier layer between the cast alloy and the die material, and acts as a release agent is also in casting ejection. The lubricant also cools down the die after ejection and prepares it for the next cycle. Although the above are believed to be helpful in reducing the soldering, their effect is limited. The reason for this is that the thin barrier film firstly forms in limited temperature range. If the die surface is very hot or very cold the barrier film might not form and secondly the film can be easily broken by the high speed injection of molten aluminium alloy, and in particular by the solidified particles.

Surface engineering is the most popular and effective way of reducing soldering in high pressure die casting of aluminium. All reported methods, Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD), Plasma assisted Chemical Vapour Deposition (PCVD), Thermal Reactive Deposition (TRD) and Laser application including Cladding, Glazing, Laser Shock Peening (LSP) were helpful to reduce corrosion and wear of the die and therefore, reduce the soldering. By means of the above mentioned methods, coatings are formed on the die surface either as a diffusion barrier and/or as a protecting coating for the melt injection. Summarized below are the features of each surfacing method.

2.5.1 Oxide coatings

It has been shown by Fraser et al. [23, 28] that an oxide coating reduced the formation of intermetallic layer on the die surface in both the dipping tests and high pressure die casting experiments. Norstrom [73] studied different oxidation procedures and found that
water steam oxidation performed very well in reducing the loss of die material after reaction with molten aluminium, Figure 2-9.

The first systematic study on the effects of oxide coating, however, was carried out by Fraser and Jahedi [23,28]. They oxidised different materials (H13, Incoloy MA956 as well as pure iron) at different conditions producing different oxide coatings. They found that air oxidation coating was porous and formed cone shape intermetallic compounds during immersion test in Al-Si-Cu alloy, indicating that this porous coating had poor soldering resistance. Steam and gas oxidation processes were adopted during further studies. The increased oxidation rate of H13 samples was obtained using steam tempering method [23]. Two oxide phases were identified: the Hematite ($\text{Fe}_2\text{O}_3$) outer oxide layer and the Magnetite ($\text{Fe}_3\text{O}_4$) inner oxide layer. The oxidized samples were dipped into the Al-11Si-3Cu alloy at 680°C and no intermetallic was found on the surface of the sample.

Figure 2-9. Weight loss of H13 with different surface modification after 4 hours exposure in Al-10%Si-08%Fe melt at 735°C [73].

It was also found [23] that after 10 minutes of immersion in Al-11Si-3Cu alloy, the oxide coatings transformed from Magnetite ($\text{Fe}_3\text{O}_4$) to Wustite ($\text{FeO}$), which is preferentially
<100> oriented. The same coating transformed to a stoichiometric form of Magnetite, Maghemite (γFe₂O₃), which indicated the chemical stability of Magnetite.

With gas oxidation, a pure Magnetite coating was formed on the H13 surface and after a 180 minutes immersion test the oxide coating was intact.

A more thermodynamically stable oxide coating, Al₂O₃, was obtained by oxidation of Incoloy MA956 tool steel. This coating was also very compact and uniform. Immersion test showed that this coating was also intact after 180 minutes.

Following the immersion tests, the resistance of oxide coating were tested in high pressure die casting using a specially designed die with removable core pin. It was found that Magnetite not only reduced soldering but was also very stable. Its stability is described in Figure 2-10[23].

![Figure 2-10. Oxidation treatment of H13 and stability of Magnetite [23]](image-url)
Fraser [28] and Gulizia [8] also mentioned the non-reactive soldering in which aluminium alloy sticks to the die/core pin surface without the formation of intermetallic. In this case, the mechanical attachment instead of the chemical bonding plays the major role in soldering and this soldering layer can be removed without damaging the die [8].

2.5.2 PVD, CVD and TRD coatings

Physical Vapour Deposition (PVD) and Chemical Vapour Deposition (CVD) are two important methods of obtaining coatings on engineering surfaces. According to Tyrkiel [74], PVD is defined as 'any vacuum deposition process whereby one of the constituents of the final coating is vaporised or atomised from the solid state within the vacuum chamber, prior to deposition'. CVD is defined as 'a reactive gas phase deposition process in which one of the reactants (typically a metal halide) is in the vapour state, prior to admittance into the reaction chamber'. Thermal Reactive Deposition and Diffusion, TRD, as was described by Arai [11], is a metallurgical process using simple heat treatment furnace.

The application of PVD or CVD coatings is the most common method to reduce or prevent soldering in aluminium high pressure die casting [8,9,18,44,75-77]. Because the soldering process involves high molten metal injection rate impingement, high temperature environment, high affinity between iron and aluminium melt, and repeated thermal cycling, it is important for the coatings to possess properties which can withstand these severe conditions. Hardness, surface roughness, thermal stability, binding stability between the coating and substrate, and compactness are usually considered as factors which play important roles in this process.

Gopal [76] investigated the effect of thin coatings in preventing soldering of A308 aluminium alloy using both accelerated soldering (dipping and rotating the sample in the aluminium alloy melt, also known as dynamic immersion test) and high pressure die casting process. They used weight loss of sample to evaluate the coatings anti-soldering effect after removing the soldered layer from the coupon surface. Although all CVD and PVD coatings helped to decrease soldering, their performance was not the same under
both testing conditions, except the vanadium carbide PVD coating which performed best in both dipping and die casting trials. Two extreme examples were CrC coating and thin ion nitrided (80-130µm) treatment. In the accelerated test, CrC was ranked 3, VC was ranked 2 and ion nitride ranked 1, while in high pressure die casting conditions, the CrC ranked 1, VC was ranked 2, thick ion nitride (150-200µm) coating and CrN were ranked 3 and thin ion nitride ranked 4, the worst. One of the reasons for the anomalous behaviour of CrC could be that the actual temperature of the H13 core in die casting is lower than that experienced in the dipping test. The substrate material experienced different exposure time to the high temperature melt. In the dipping test this period was much longer than that in the real high pressure die casting. CrC has higher oxidation temperature so that it performed better. The author did not give any explanation for the anomalous performance of nitride coating. A possible reason is that the hardness of this coating is not high enough (746HV) compared to that of CrC (1850HV) to withstand the high molten metal impingement including the erosive wear from particles precipitated from the molten metal.

PVD Cr-based coatings are well known for their high oxidation temperature, which is two times higher than that of the TiN. Aluminium addition in TiN and CrN can improve the oxidation property [78,79]. Wang [9] tested H series tool steels and two maraging hot work tool steels for their performance under coated condition in die casting. All samples were coated with TiN, TiAlN, and CrN deposited via a steered arc evaporation process applied at 400-450°C. It was found that all three coatings have some effect in helping to reduce the die softening after thermal cycles. The coatings did not increase the heat checking resistance, on the contrary, they reduced it on some materials. This may reflect the problem of the adhesion between the coating and the substrate. TiN did not last long because of its low oxidation temperature.

Yan and Fan [45] used Cr₂O₃ on the surface of H21 tool steel in a dipping test into A380 alloy and found that although this coating would protect the substrate to some extent from erosion, it acts only as a diffusion barrier because the coating itself was attacked by molten Al-alloy through chemical dissolution.
By observing the casting alloy build-up layer on top of PVD coating, Gulizia [8] proposed another soldering mechanism, mechanical soldering. The build-up alloy appeared during die casting but was removed in the following shots. This build-up may cause some defects on few castings but won’t damage the die because there was no chemical bonding between the build-up and the die.

2.5.3 Comparison of coating methods

Common CVD methods involve high temperature (1000°C) on the coating substrate which may cause its deformation. Plasma assisted CVD (PCVD or PACVD) may reduce the reaction temperature (around 500°C) and keep the high reaction rate of the CVD method. PVD often works at temperature <400°C which is better for the substrate. TRD can work at a wider temperature range. The main coatings are V and Cr carbonised coatings. Table 2-3 gives some idea of how the coatings and their deposition methods have been adopted by industry [12].

Table 2-3. Industry survey on the use of coatings in die casting [12]

<table>
<thead>
<tr>
<th>Detail</th>
<th>Number of companies</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Survey response/sent</strong></td>
<td></td>
</tr>
<tr>
<td>Die casting companies</td>
<td>31/53</td>
</tr>
<tr>
<td>Coating companies</td>
<td>3/4</td>
</tr>
<tr>
<td><strong>Major component manufactured</strong></td>
<td></td>
</tr>
<tr>
<td>Auto part</td>
<td>20</td>
</tr>
<tr>
<td>Others</td>
<td>11</td>
</tr>
<tr>
<td><strong>Substrate materials</strong></td>
<td></td>
</tr>
<tr>
<td>Premium H13</td>
<td>11</td>
</tr>
<tr>
<td>H13</td>
<td>20</td>
</tr>
<tr>
<td><strong>Production Volume</strong></td>
<td></td>
</tr>
<tr>
<td>Up to 100,000</td>
<td>14</td>
</tr>
<tr>
<td>&gt;100,000</td>
<td>6</td>
</tr>
<tr>
<td><strong>Coating used</strong></td>
<td></td>
</tr>
<tr>
<td>CrC</td>
<td>12</td>
</tr>
<tr>
<td>CrN</td>
<td>10</td>
</tr>
<tr>
<td>TiN</td>
<td>5</td>
</tr>
<tr>
<td>TiAlN</td>
<td>4</td>
</tr>
<tr>
<td>VC</td>
<td>1</td>
</tr>
<tr>
<td>Others</td>
<td>1</td>
</tr>
</tbody>
</table>

*One company reported significant improvement in wear resistance by the use of double coatings*
Table 2-4 is a brief summary of the coatings applied in the prevention of soldering. Although all the applied coatings enhanced the anti-soldering properties of the die materials, it is difficult to evaluate the effects of coatings quantitatively. Firstly, the coating method is different. As an example, TiN coating is one of the most popular coatings which can be achieved from various CVD and PVD techniques. These different methods, with different deposition conditions (pressure, temperature, growth rate, pretreatment, substrate condition, etc) can produce TiN with different physical properties, such as hardness and surface roughness. Secondly, the casting and its process details can be different. The alloy composition, injection speed, casting wall thickness, alloy temperature, and cooling conditions can change from product to product. Thirdly, the evaluation methods could be different.

Two trends are clear from Table 2-4. One is laser surface treatment and the other is the multilayer system. Laser surface engineering is a very attractive technique owing to its flexibility, its nonequilibrium processing capabilities (involving high solidification rates up to $10^3$-$10^8$Ks$^{-1}$), and its ability to increase the solid solubility limit beyond the equilibrium phase diagram. The laser produced coating is metallurgically bonded to the substrate which provides better adhesion [75]. Single coating can not eliminate soldering completely. Some coatings have good resistance to aluminium alloy but have poor thermal shock resistance. Others have good thermal fatigue resistance and excellent compatibility of the thermal expansion coefficient with substrate, but have poor corrosion and erosion resistance. Multilayer consideration combines the advantages of each single coating in preventing soldering. Figure 2-11 shows one design model and concept of a multiple coating.
<table>
<thead>
<tr>
<th>Author(s)</th>
<th>Substrate</th>
<th>Experimental method</th>
<th>Alloy, temperature</th>
<th>Examined coatings</th>
<th>Best Result(s)</th>
<th>Note (Evaluation Method)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[76]</td>
<td>H13 (PVD)</td>
<td>Dynamic Dipping</td>
<td>A380, 680°C</td>
<td>CrN1, CrC, BC, VC, IN1-Thicker, IN2-thinner, Shot-peening+CrN2</td>
<td>VC, CrN1</td>
<td>Weight loss</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HPDC</td>
<td></td>
<td></td>
<td>CrC, VC</td>
<td></td>
</tr>
<tr>
<td>[8]</td>
<td>H13 (PVD)</td>
<td>Both accelerated and HPDC production</td>
<td>ADC12</td>
<td>TiCN, Nitrided plus all coatings of two different thickness and microblasted</td>
<td>TiN, CrN</td>
<td>Soldering and build-up covered area percentage Roughness effect</td>
</tr>
<tr>
<td>[9]</td>
<td>5 different materials including H10, H13, H19, etc and PVD</td>
<td>N/A, (heat checking experiment)</td>
<td></td>
<td></td>
<td>TiAIN, CrN, TiN</td>
<td>Evaluated with mapping the corrosion area and depth. Oxidation temperature affect the corrosion</td>
</tr>
<tr>
<td>[78]</td>
<td>H11 (PVD)</td>
<td>Electrolytic corrosion in a die lubricant environment</td>
<td>(Cr58, Al42)N, CrCN, CrN, CrN Plasma nitrided</td>
<td>(Ti56, Al44)N</td>
<td></td>
<td>Current density, Rest &amp; broken down potential</td>
</tr>
<tr>
<td>[75]</td>
<td>H13 (laser surface treatment)</td>
<td>Both static and dynamic dipping</td>
<td>A390, 670°C</td>
<td>Laser Glazing, 2μmTiC</td>
<td>Laser shocked, 0.3μmTiC</td>
<td>Weight loss, 2μmTiC is better in static than Laser glazing, while glazing is better in dynamic, LSP not tested dynamically</td>
</tr>
<tr>
<td>[77]</td>
<td>Review</td>
<td>HPDC</td>
<td>TiN+TiCN+TiN, TiN, TiC+TiN</td>
<td>TiBN</td>
<td>TiBN, did not fail after 30,000 shots</td>
<td></td>
</tr>
<tr>
<td>[13]</td>
<td>Laser cladding</td>
<td>Dipping</td>
<td>Ni, WCNi, BN/NC, VC, VC/NCi(50%-50%, and 10%-90% fractions), Ti on Ti, Hastelloy C</td>
<td>W/Fe, W</td>
<td>No significant reaction after three hours</td>
<td></td>
</tr>
<tr>
<td>[80]</td>
<td>PVD</td>
<td>Dynamic dipping</td>
<td>A390, 710C</td>
<td>ZrN, TiAIN,AlTiN</td>
<td>CrN, TiN</td>
<td>Weight loss</td>
</tr>
</tbody>
</table>
Another trend is the application of laser surface treatment through cladding, surface reaction, shot peening etc. The laser coated 0.3μm TiC showed very promising effects on prevention of the intermetallic growth under both static and dynamic conditions [75]. It is interesting that under static condition, the 2 micron TiC coating sample performed better than the laser glazed sample, but under dynamic condition, the laser glazed sample performed better. It is believed that this was due to the lower surface roughness of the glazed sample which led to lower stress concentration. This raises a question on the effect of surface roughness on the intermetallic formation in high pressure die casting. Gulizia investigated this effect and found that the roughness condition made no contribution to soldering formation [8], but Arai’s results [11] showed that die life was highly related to the surface roughness, warpage and coating thickness.

One of the most attractive techniques in anti-soldering studies was the laser shock process. Under static condition, this sample performed as well as the 0.3micron TiC laser coated sample, which was the best in Pirzada's experiment [75]. Unfortunately, Pirzada didn't give any further information on processing details and dynamic testing was not performed. Brandt's study on anti-soldering coatings using laser cladding also gave a satisfactory result [13].
2.5.4 Failure modes of the coatings

Three failure modes, as shown in Figure 2-12 [18,35,81-85], dominate in the failure of coatings in high pressure die casting: cracking, diffusion and surface defect. Cracking of the coating occurs mainly because of thermal expansion. This happens when there is a mismatch of the coefficient of thermal expansion (CTE) between the coating and the substrate material, especially when the coating is subjected to higher temperature and thermal cycles, similar to those occurring in high pressure die casting. The coating cracks either because of tensile or compressive stress. After cracking, the corrosion and erosion occurs at the cracking spot where the alloy melt and die steel contact directly. Diffusion occurs especially when the coating has a columnar structure and the molten casting alloy diffuses into the die steel through the grain boundary. From this point of view, an amorphous coating would perform better. Surface defects were produced on the coating during the deposition. The defects in the PVD coating process are very common if the substrate is not prepared properly or if the target is not homogenous. Defects usually are particles and/or core pin holes on the coating. During die casting, this coating fails to protect the die steel from reacting with the alloy melt.

Therefore, the research and development of a coating system for application in high pressure die casting involves finding a material and a process that can reduce or eliminate the possibility of failure so as to fully protect the die surface.
2.6 Summary

This chapter reviewed literature relating to the soldering in high pressure die casting of aluminium alloys and the metallurgical aspects which may lead to soldering in magnesium high pressure die casting.

The soldering in high pressure die casting of aluminium is mainly due to the strong affinity of aluminium for iron. In magnesium high pressure die casting, the affinity is not between magnesium and iron but still aluminium, the major alloying element of the magnesium alloys and the die material, iron. Thus there is the possibility of formation of the Fe-Al intermetallic. Because of the different aluminium content in the molten magnesium alloys the intermetallic formation mechanism may vary.

For magnesium alloys, e.g. AZ91D, the casting skin has a high aluminium content. This increases the combined properties in this area but also provide a chance of the intermetallic reaction at the interface vicinity. Al-Fe-Mn is another important system which may influence reactions at the interface. With different aluminium content in the
alloy, iron and manganese show different solubility. All these effects need to be verified in experiments and the dip test is the most suitable method.

The effect of surface engineering on reducing the soldering in aluminium high pressure die casting was also reviewed. Based on literature, PVD TiN and CrN are the most popular coatings applied to reduce soldering in aluminium high pressure die casting. Laser cladding and oxide coatings had also demonstrated good resistance to soldering. The effect of these coatings on the reduction of soldering in magnesium die casting needs to be investigated.
Chapter 3 Experimental Methodology

3.1 Understanding of the soldering mechanism in high pressure die casting of magnesium alloys

The investigation of the soldering mechanism was carried out using two methods. The first method was the dipping or immersion test. This method is widely accepted as a way of simulating it [10,17,22,44,86]. It involves immersing a prepared H13 tool steel sample into a molten magnesium alloy for a certain period of time ranging from 5 minutes to 6 hours. During this immersion, intermetallic may form on the sample surface. Understanding of the formation mechanism of intermetallic under different alloy condition can contribute to the understanding of soldering mechanism in high pressure die casting.

A preliminary dipping test with H13 samples was carried out in AZ91D to understand the factors which affect the formation of intermetallic phase and lead to soldering. Based on these results, a series of dipping tests was designed and carried out to further understand the soldering mechanism.

The second method, which is also widely accepted in aluminium soldering research [17,23,31,37,40], is the accelerated die casting using a specially designed die. This process can greatly reduce the number of shots before obtaining a soldering layer. Thus combining the results from dipping tests and accelerated high pressure die casting trials can lead to better understanding of the soldering in high pressure die casting of magnesium alloys.

To prevent soldering, surface engineering, including PVD of thin films, plasma nitriding, oxide coating and laser cladding of Fe+W in a ratio of 50%+50% were tested in the most serious soldering conditions.
3.1.1 Dipping tests

3.1.1.1 Materials used in experiments

H13 tool steel was selected as die steel for all experiments. Its chemical composition is shown in Table 3-1. For the dipping tests, H13 tool steel samples of size 25x25x3mm were prepared and heat treated [87] then polished with #1200 SiC paper. The samples were then cleaned with ethanol, and kept in an argon filled container on top of the dipping furnace for preheating (~250ºC) before dipping into the melt. A hole was drilled in each sample to hang it into the alloy melt.

Table 3-1. H13 tool steel composition

<table>
<thead>
<tr>
<th>Cr</th>
<th>Si</th>
<th>Mo</th>
<th>C</th>
<th>Mn</th>
<th>V</th>
<th>Others</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.9</td>
<td>1.01</td>
<td>1.35</td>
<td>0.38</td>
<td>0.42</td>
<td>0.92</td>
<td>&lt;0.4</td>
<td>Balance</td>
</tr>
</tbody>
</table>

For the preliminary dipping tests, AZ91D magnesium alloy was selected because it is the most widely used alloy in high pressure die casting [63,64]. Its nominal composition is listed in Table 3-2.

Table 3-2. Composition of AZ91D used in the preliminary dipping test

<table>
<thead>
<tr>
<th>Al</th>
<th>Mn</th>
<th>Zn</th>
<th>Si</th>
<th>Others (Cu, Ni, Fe)</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.88</td>
<td>0.104</td>
<td>0.90</td>
<td>0.011</td>
<td>&lt;0.005</td>
<td>Balance</td>
</tr>
</tbody>
</table>

From preliminary tests, it was found that aluminium and manganese are two of the critical elements in magnesium alloy for the formation of intermetallic phase which can lead to soldering. Thus two groups of magnesium alloys were made to investigate the role of these two elements in the soldering reaction. The first group was alloyed with aluminium ranging from 3 wt.% to 12 wt.% to investigate the role of aluminium and the second group was alloyed with 3 wt.% of aluminium as well as manganese ranging from 0.178 wt.% to 0.520 wt.. Details of the alloy compositions are listed in Table 3-3. Commercially pure magnesium (>99.95%) and aluminum (>99.8) ingots were supplied by Sims Aluminium and Nonferral Pty. Ltd. Australia respectively. Their certified
compositions are shown in Table 3-4 and Table 3-5. Manganese was added in the form of 40%Mn-60%Al master alloy to Mg which was alloyed with a certain amount of aluminium. All ingots and alloy compositions were determined using a ‘SPECTRO’ element analysis machine and each result is the average of seven spark readings.

Table 3-3. Magnesium alloys used for the dipping test to investigate the role of aluminium and manganese in the soldering reactions

<table>
<thead>
<tr>
<th>Element</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
<th>#5</th>
<th>#6</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>3.192</td>
<td>5.94</td>
<td>11.7</td>
<td>2.978</td>
<td>2.983</td>
<td>2.793</td>
</tr>
<tr>
<td>Mn</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>0.178</td>
<td>0.362</td>
<td>0.520</td>
</tr>
</tbody>
</table>

Table 3-4. Magnesium ingot composition

<table>
<thead>
<tr>
<th>Mg</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Al</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.9547</td>
<td>0.00145</td>
<td>0.00116</td>
<td>0.0024</td>
<td>0.00062</td>
<td>0.001</td>
<td>0.0093</td>
<td>0.0295</td>
</tr>
</tbody>
</table>

Table 3-5. Aluminium ingot composition

<table>
<thead>
<tr>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
<th>Cu</th>
<th>Mn</th>
<th>Ni</th>
<th>Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td>99.82</td>
<td>0.115</td>
<td>0.035</td>
<td>0.0025</td>
<td>0.0025</td>
<td>0.005</td>
<td>0.001</td>
</tr>
</tbody>
</table>

3.1.1.2 Dipping test furnace design

The dipping tests were performed using a specially designed furnace, as shown in Figure 3-1, with nickel free mild steel crucible for the melting of magnesium alloys. To prevent exothermic reactions, AZ91D ingots were cut and preheated before melting. Preheating of the ingot removes moisture absorbed by the alloy and/or by Mg oxide product (MgO) on its surface so that it is safe when it is melting.
The selection of nickel free mild steel as the crucible material was based on the fact that nickel may contaminate the melt and mild steel does not have affinity for magnesium. In this case a clean magnesium alloy can be ensured. The crucible was CIG welded rather than MIG welded so that the copper coating on the welding electrode did not contaminate the alloy. The crucible was designed to hold ~3 kg of magnesium alloy.

The crucible was checked for cracks before each experiment. An induction pan was also designed and placed underneath the crucible for preventing any leaking magnesium getting into direct contact with refractory materials. The safety arrangement of the magnesium alloying furnace is shown in Figure 3-2.
3.1.1.3 Dipping tests procedure

H13 samples with hardness of 46-49 HRC were prepared and ground with 1200 mesh SiC paper to remove any oxide coating. The samples were then put in a container filled with argon and placed on top of the furnace for preheating.

The magnesium alloy in the crucible was preheated up to 300°C for over 30 minutes and then the cover gas was turned on and the ingot was heated to the preset temperature of 680°C. During this procedure, the aluminium ingots were also heated on top of the furnace. The cover gas flow rate was determined according to the empty volume in the crucible. It was usually three times this volume per minute. Aluminium ingot was then added into the melt to obtain the desired composition of the Mg-Al alloy. Melt was stirred with an iron bar before alloy sample was taken from the melt and analysed to make sure the alloy composition was correct. To make Mg-3%Al-Mn alloys, Al-Mn master alloy was added to the melt, stirred and held for 1-2 hours before a sample was taken.
The dipping samples were quickly removed from the argon filled container suspended with a steel wire from the hanging bar and immersed into the melt. The melt was kept at 680±1°C during immersion and stirred regularly. Immersed samples were kept in the melt for a certain period of time and then removed and quickly covered with dry sand to cool them down and prevent them from burning. The samples were then ready for metallurgical analysis.

### 3.1.2 Die casting

A specially designed die [17,23,40] was used to perform the die casting trials with AZ91D alloy, Figure 3-3. A feature of this die is its block shape which gives the casting a longer time to solidify and greater chance for the intermetallic reaction to take place in addition to the usual injection impingement. The second feature is that its core pin was placed facing the injection gate which gives the core pin surface immense impingement which leads to the quick formation of the intermetallic. This is demonstrated effectively in the soldering process in high pressure die casting of aluminium[17].

To study the effect of the temperature on the soldering reactions, one of the core pins was machined to fit a thermocouple at its tip so as to obtain temperature data in the core pin. The structure of the core pin is shown in Figure 3-3b. It has been demonstrated in aluminium die casting that the temperature in this position is about the same as in direct contact with the alloy [17].

A 250 ton Toshiba high pressure die casting machine at CSIRO was used for the experiments. Alloy temperature in the crucible was maintained at 680°C and a mixture of 0.18%SF₆ + N₂ was used as the cover gas. To accelerate the soldering reaction, the machine was subjected to its extreme operating conditions of injection speed (>80m/s), cycle time (55s) and holding pressure (>1000kg). Manual coolant spray was used between casting shots and only applied to the die surface so as to obtain soldering layer on the core pin as quickly as possible.

A data acquisition unit was used to monitor the temperature change of the core pin, Figure 3-4.
Figure 3-3. High pressure die casting die cavity. a) Position of the core pin, b) dimension of the core pin with thermocouple hole.

The typical temperature change is shown in Figure 3-5. It is seen that the peak core pin temperature is changing periodically reflecting the build-up of intermetallic and casting alloy on its surface. Higher temperature was observed when the build-up layer was
cleared away by the following few shots. The highest temperature reached was about 575°C.

Figure 3-4. The Data Acquisition Unit

Figure 3-5. Core pin temperature profile for 6 cycles
3.2 Coatings for soldering prevention

3.2.1 Oxide coating

The iron oxide coating was produced in a gas mixture of \( \text{CO}_2/\text{H}_2 \) in a 95:5 ratio at 550°C for 2 hours. The oxide coating thickness was approximately 3\( \mu \)m, Figure 3-6, and it was pure magnetite, \( \text{Fe}_3\text{O}_4 \) (JCPDF 75-33), Figure 3-7. The same coating remained intact after testing in 680°C molten Al-11Si-3Cu alloy for 3 hour [23,28].

Figure 3-6 Magnetite coating on H13 substrate
3.2.2 Nitriding

Nitriding was carried out using NitroPlas at Surface Technology Coatings Pty. Ltd, Australia. The NitroPlas system generates plasma on a cage surrounding the entire workload which is placed in a vacuum furnace. The created active nitrogen penetrates the component’s surface and reacts with the alloying elements in the steel to produce a nitrided structure which is harder and has improved ductility and fatigue resistance compared with gas and salt bath nitriding. The system is shown in Figure 3-8 and a cross-section of a nitrided sample is shown in Figure 3-9. The total nitrided coating thickness exceeded 100µm and a white layer of 3-4 µm thick was formed on the sample surface. Other than the white layer (Fe$_3$N, JCPDF #76-91 and Fe$_4$N, JCPDF #83-231), CrN was present in the sample surface XRD pattern, Figure 3-10.
Figure 3-8. Nitroplas system

Figure 3-9. Cross section of nitrided sample showing the white and diffusion layers.
Sample was etched
3.2.3 Laser cladding of tungsten coating

Cladding of mixture of iron and tungsten powders was carried out on a Rofin Sinar 2.5 kW, optical fibre delivered Nd:YAG laser located at Swinburne University of Technology. This laser system is capable of operating both in continuous mode (CW) and pulse mode. The continuous mode was used in this trial. The cladding set up is shown in Figure 3-11.

A mixture of tungsten and iron powders in a 50 wt.% ratio was applied to the laser spot on the workpiece through the powder delivery nozzle. The powder nozzle was surrounded by a shielding gas nozzle so as to protect the melt pool from oxidation. By selecting cladding parameters, such as laser power, scanning speed, and powder dosing rate, the optimum cladding condition was achieved which led to the production of uniform coating with good adhesion to the substrate. In this experiment, a coating thickness of over 700µm was obtained, Figure 3-12.

Figure 3-10 XRD pattern of the nitrided surface
Figure 3-11. Laser cladding set up

Figure 3-12. Microstructure of W/Fe clad coating on H13 tool steel
3.2.4 Physical vapor deposition

PVD coatings were prepared on samples with one side finely ground with 600 mesh SiC paper and the other side left as machined.

Physical vapour deposition was carried out on a random cathodic arc deposition system as shown in Figure 3-13. This system comprises 6 vertically mounted cathodic arc sources. Samples were etched with argon ions for 30 minutes under 5 Pa pressure and 1000 V biased potential. This was followed by metal ion etching at biased potential of 800 V and 0.8 Pa pressure before coating. Ti was used for TiN coating and Cr was selected for CrN coating as targets. Samples were then coated under nitrogen pressure of 0.7 Pa for 40 minutes with biased potential of 200 V.

For the composite coatings of CrN/TiN/Nitride, direct deposition of coatings was carried out on the nitried substrate.

Figure 3-13. Random Cathodic Arc PVD system
The coated sample surfaces are shown in Figure 3-14. It can be seen that macro-particles and pinholes were present on the surface for both TiN, JCPDF #87-633 and CrN, JCPDF #11-65 coatings, as shown in Figure 3-15 and Figure 3-16, respectively. TiN coating on all samples had a thickness of approximately 1-1.5 µm and CrN approximately 2µm.

Figure 3-14. Pinholes and macroparticles on the surfaces of PVD coatings. a) TiN, b) CrN

Figure 3-15 XRD pattern of the PVD TiN coating
3.3 Characterization and sample preparation

All dipped samples and die cast pins were metallurgically analysed. For the morphology analysis, optical microscope and a Leica S440 Scanning Electron Microscope (SEM) were used. Semi-quantitative compositional analysis of the elements in intermetallic phases was carried out using Leica S440 fitted with a Link Ge EDX (Energy Dispersive Spectroscopy) detector and Link ISIS software. For the phase analysis, X-Ray Diffraction techniques (XRD) were carried out on a Siemens D500 with CuKα₁ radiation, $\lambda=1.54056\text{Å}$. X-ray micro-diffraction using a Bruker General Area Detector Diffraction System (GADDS) [88] was also used to identify phases, especially phase changes from the substrate to soldering alloy.

Figure 3-16 XRD pattern of the PVD CrN coating
3.3.1 Polishing

Sectioned samples were mounted and polished using specially developed polishing process. As is widely known, magnesium alloys with iron contamination have very poor corrosion resistance. During the preparation of samples, it was found that because there was a rather high iron content at the intermetallic-soldering alloy interface, it was hard to get a clean polished interface because of the corrosion. All the conventional polishing agents were water based which enhanced this problem.

The newly developed polishing process was as follow:

1. Grinding the samples to 600 mesh with SiC paper using water as lubricant/coolant,

2. Fine grinding to 1200 mesh with ethanol as lubricant/coolant,

3. Applying 3µm diamond paste to polishing pad, intermittently apply olive oil as lubricant and polish for 3 minutes at 30N pressing force. Then immediately clean with ethanol.

4. Repeat step 3 with 1µm diamond paste.

5. If samples were to be SEM/EDX analyzed, gold/carbon coating was applied immediately.

Because the intermetallic layers formed on some of the samples were too thin to be used for phase scans, even with GADDS, the tapered polishing technique was adopted to overcome this problem. With this technique, samples were cut at an angle rather than perpendicular to the sample surface. Mounting and polishing this angled section resulted in an enlarged sample area which made the analysis considerably easier.

3.3.2 Removal of the cast alloy overlay

To obtain the surface morphology of intermetallic phase, the magnesium alloy on top of the intermetallic layer was removed by SnCl₂ etchant. This solution was originally used
to remove aluminium alloys without affecting the underlying intermetallic phase[23]. The solution was made by dissolving 100g hydrated stannous chloride in 50 ml of 50% warm hydrochloric acid. The solution was diluted with 100g of distilled water and 1g of metallic tin was added. The solution was further diluted, in the ratio of 1:9, with distilled water. The soldering sample was then immersed into the solution and the reaction products were removed lightly with a brush. It is noted that a small amount of tin may deposit on the sample surface and appears on SEM and especially XRD patterns. This was noted during the identification of phases.

A disadvantage of this etchant is that it removes the Mn-Al build-up particles in the matrix of Al-rich magnesium. This caused difficulty in obtaining the surface morphology of this layer. The typical intermetallic morphology using this etchant from a sample dipped into Mg-12%Al alloy is shown in Figure 3-17.

Figure 3-17. Intermetallic morphology obtained from dipping sample in Mg-12%Al after alloy overlay was removed with the SnCl₂ etchant
3.4 Summary

This chapter introduced the experimental methodology used to investigate soldering in magnesium high pressure die casting and its prevention with surface engineering.

The dip test was adopted as the key method for investigating reactions between the magnesium alloys and H13 substrate. Different aluminium and manganese contents were alloyed into magnesium so as to investigate their roles in the intermetallic reaction. The results are going to be compared with and verified in die casting trials using a specially designed die. Surface coatings and treatments will be developed and tested mainly in the dipping test.

All samples are to be analysed at their cross-sections and/or surfaces by means of scanning electron and optical microscopes, and x-ray diffraction/x-ray micro-diffraction techniques, the later is especially advantageous in identifying phases at a very small spot and phase changes along certain direction.
Chapter 4  Experimental Results

This chapter presents a series of results relating to the dipping test and die casting trial. The preliminary dipping test in AZ91D revealed that aluminium, iron and manganese were the three elements involved in the formation of the intermetallic layer, therefore, magnesium alloys with different aluminium and manganese contents were produced to carry out the dip test. This leads to the understanding of the roles of each element in the intermetallic reaction. Die casting trial followed and its results are compared with those of the dipping test so as to fully understand the soldering phenomenon.

4.1 Dipping tests

The dipping experiments were designed to understand the factors governing soldering of magnesium alloys and to produce deeper understanding of the soldering reactions occurring in high pressure die casting. They were also aimed at identifying potential surfacing technology which could prevent it.

4.2 AZ91D dipping tests

4.2.1 Intermetallic layer morphology

H13 samples were prepared according to the procedures explained in section 3.1.1. These samples were dipped into the AZ91D melt at 680°C for a period of 5, 15, 45, 60, 120 and 180 minutes respectively. The results are shown in Figure 4-1.

It is clear from Figure 4-1 that an intermetallic layer was produced with all samples. This intermetallic has the following features. Firstly, it formed a layer between the substrate and the alloy, and its thickness increased with dipping time. Secondly, it comprises two layers: the layer next to the magnesium alloy, termed the outer layer which appears bright in colour, and the darker layer next to the H13 substrate, termed the inner layer. The inner layer has darker appearance and is divided by some lighter column-like intermetallic, Figure 4-1e.
The third feature is that the differently coloured intermetallic has a different composition. EDX point scan showed that all the intermetallics are composed of aluminium, iron, and manganese, as given in Table 4-1. Only very small amounts of silicon, vanadium and chromium were detected.

![Microstructures of samples dipped into AZ91D alloy for 5, 15, 45, 60, 120 and 180 minutes respectively (a-f)](image)

Figure 4-1. Microstructures of samples dipped into AZ91D alloy for 5, 15, 45, 60, 120 and 180 minutes respectively (a-f)
Removal of the soldered magnesium alloy allows the surface of the outer layer to be observed under the microscope, as shown in Figure 4-2. The different darkness in Figure 4-2 corresponds to the sectioned image shown in Figure 4-1e.

Figure 4-2. Surface of the outer intermetallic layer from sample dipped into AZ91D for 120 minutes

Table 4-1. Intermetallic composition of three different areas (at.%) marked in Figure 4-1e

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Others (Mg, Cr, Si, etc)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase 1</td>
<td>66.9</td>
<td>13.8</td>
<td>17.09</td>
<td>Balance</td>
</tr>
<tr>
<td>Phase 2</td>
<td>71.42</td>
<td>15.88</td>
<td>11.55</td>
<td>Balance</td>
</tr>
<tr>
<td>Phase 3</td>
<td>63.08</td>
<td>13.08</td>
<td>21.76</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The relationship between the intermetallic thickness and dipping time is shown in Figure 4-3. The intermetallic thickness increased from 1.5 µm to 14.3 µm with an increase in the
dipping time from 15 minutes to 180 minutes. It is also clear that this relationship is linear.

![Graph showing thickness of intermetallic layer as a function of dipping time](image)

Figure 4-3. Thickness of intermetallic layer as a function of dipping time for H13 samples in molten AZ91D

### 4.2.2 Intermetallic phase identification

X-Ray diffraction pattern of the intermetallic formed in AZ91D is shown in Figure 4-4. Based on this and the intermetallic composition in Table 4-1, the following phases were identified. The inner layer was orthorhombic $\eta$-Fe$_2$Al$_5$ (JCPDF #47-1435), no Al-Mn binary phase was identified in this area. The outer layer was mainly Mn$_5$Al$_8$ phase (JCPDF #49-1279). It appears that the manganese in the inner layer acted as a substitutes for the Fe. The ferrite in the substrate (JCPDF # 6-696) also appeared in the pattern. There were some unidentified peaks on the pattern which it is believed belong to an intermediate phase of Al-Fe-Mn.

The red lines in the pattern represent the position of the weak peaks of Sn (JCPDF #4-673) deposited during etching with SnCl$_2$. 
4.3 Mg-Al alloys dipping tests

4.3.1 Intermetallic layer morphology

Illustrated in Figure 4-5 to Figure 4-7 are the cross-sections and surface morphologies of samples dipped into the magnesium alloys with different aluminium content for 5, 30, 60 and 180 minutes respectively. Under SEM, it is hard to identify the intermetallic layer on the samples dipped into both Mg-3\%Al and Mg-6\%Al alloys, however, there were some areas in the Mg-6\%Al alloy which were covered with intermetallic particles. Intermetallic layer became very thick (>250\(\mu\)m) on samples dipped into the Mg-12\% alloy for 2 and 3 hours.
Figure 4-5. Intermetallic phases on H13 steel dipped into Mg-3%Al alloy (Alloy #1). a), c), e) and g) are sectioned images of samples dipped for 5, 30, 60 and 180 minutes respectively. b), d), f) and h) are corresponding surface morphologies after magnesium alloy overlays were removed by SnCl₂ etchant.
Figure 4-6. Intermetallic phases on H13 steel dipped into Mg-6%Al alloy (Alloy #2). a), c), e) and g) are sectioned sample images dipped for 5, 30, 60 and 180 minutes respectively. b), d), f) and h) are the corresponding surface morphologies after magnesium alloy overlays were removed by SnCl₂ etchant.
Figure 4-7. Intermetallic phases on H13 steel dipped into Mg-12%Al alloy (Alloy #3). a), c), e) and g) are sectioned sample images dipped for 30, 60, 180 and prolonged 360 minutes respectively. b), d), f) and h) are the corresponding surface morphologies after magnesium alloy overlays were removed by SnCl₂ etchant.
From the images shown in Figure 4-5 to Figure 4-7 it is clear that continuous intermetallic layers were not easily formed or maintained in alloys with 3% and 6% aluminium. Pits/grooves and particles were formed on the substrate in the Mg-3%Al alloy and with increasing dipping time the particles disappeared while more pits/grooves appeared. No pits/grooves could be seen in the Mg-6%Al alloy but there were particles on the substrate surface that were ‘teeth-like’ in sectioned images (Figure 4-6a, c, e and g). These particles grew larger with time and increased aluminium content, but their density on the surface did not change much. The intermetallic layer thickness obtained from these two alloys was difficult to define because it was very thin or had not yet formed a continuous layer.

The intermetallic layer formed easily in the 12%Al-Mg alloy. Its thickness increased with time following a two-stage growth. The growth was linear from 11.72 μm at dipping time of 5 minutes to 256.2 μm at the dipping time of 180 minutes, and then it slowed down sharply, stabilizing at about 270μm between dipping time of 180 and 360 minutes. Figure 4-8 shows the intermetallic thickness as a function of dipping time in the 12%Al-Mg alloy.
4.3.2 Intermetallic phase identification

All the intermetallic particles appearing on dipping into the 3%Al-Mg alloy with the dipping times of 60 and 180 minutes showed similar EDX spectra, Figure 4-9. It appeared that in all intermetallic particles, Al and Fe were the dominant elements with small amount of Cr, V and Si coming from the H13 substrate.

![Figure 4-9. EDX spectra of intermetallic particles on the H13 surface after dipping into 3%Al-Mg for a) 60 and b) 180 minutes](image)

From the EDX point scans it was found that the intermetallic compositions are mainly classified into two groups, as given in Table 4-2. Most particles formed on the substrate had the Phase 1 (51-53 at.%Al-Fe) composition, with only a very small amount of
particles detected having the Phase 2 (63-67 at.\%Al-Fe) composition. Some areas of the substrate, where no particle was found, had a composition of 16.0-28.3 at.\% aluminium.

Table 4-2. Compositions of intermetallic found on H13 steel samples dipped into Al-Mg alloy (at.\%, Cr, V and Si as balance)

<table>
<thead>
<tr>
<th>Alloy Group 1</th>
<th></th>
<th>Al</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Alloy#1</td>
<td>53</td>
<td>42.9</td>
</tr>
<tr>
<td></td>
<td>Phase1</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Phase2</td>
<td>66.93</td>
<td>31.45</td>
</tr>
<tr>
<td></td>
<td>Phase1</td>
<td>51.16</td>
<td>47.12</td>
</tr>
<tr>
<td></td>
<td>Phase2</td>
<td>63.48</td>
<td>34.7</td>
</tr>
<tr>
<td></td>
<td>Phase3</td>
<td>70.12</td>
<td>28.89</td>
</tr>
<tr>
<td></td>
<td>Alloy#3</td>
<td>83.71</td>
<td>14.41</td>
</tr>
</tbody>
</table>

A layer, composed of Mg, Fe and O was detected in the hanging hole (the hole used for hanging the sample into the melt) from the sample dipped into 3\%Al-Mg alloy for 60 minutes, as shown in Figure 4-10. Its averaged composition was 23.2 at.\%Fe, 9.65 at.\%Mg, and around 66.9 at.\% O, with Cr as balance. Al was not detected in this layer. The thickness of this layer was approximately 20–30\μm.

Figure 4-10. Fe-Mg-O layer formed at the hanging hole
The intermetallic formed on samples dipped into the 6% Al-Mg alloy had a similar composition to that dipped into the 3% Al-Mg alloy, as shown in Phase 1 and Phase 2 in Table 4-2. A third group of intermetallic (Phase 3) appeared in this alloy and according to the Al-Fe phase diagram it was the Fe$_2$Al$_5$ phase[91].

The fast-grown intermetallic layer on samples dipped into Alloy #3 had aluminium composition ranging from 79 to 86 at.%. Some light coloured particles, composed of Al, V, Cr and Fe, were seen distributed in the main Fe-Al phase matrix, Figure 4-11.

The XRD pattern of intermetallic formed on the 3% Al-Mg samples (Figure 4-12) showed that FeAl (JCPDF #1-1275) was the major phase present, weak FeAl$_2$ (JCPDF #34-570) peaks were also observed. On samples dipped into Alloy #2, FeAl was still the major phase present (Figure 4-13) with FeAl$_2$ peaks observed similar to those observed in the case of 3% Al-Mg alloy. Fe$_2$Al$_5$ (JCPDF #47-1475) was also formed in very limited amount.
Figure 4-12. XRD pattern of intermetallic formed on H13 steel samples dipped into 3%Al-Mg alloy

The Icosahedral phase, Fe\textsubscript{14}Al\textsubscript{86} (JCPDF #39-824), was found in the 12% Al-Mg alloy (Figure 4-14) with aluminium content varying from 79 at.% to 86 at.%. and this resulted
in the d-spacing (2.115Å) different from that from the card (2.11 Å). Very weak Fe$_2$Al$_5$ peaks were also detected but the light coloured particles containing Al, Cr, V and Fe observed through EDX were not identified by XRD, Figure 4-11.

It was noted that the main Fe peaks detected were shifted in the Mg-3%Al and Mg-6%Al alloys. The shifting of FeAl peak was more significant in the case of dipping into Mg-6%Al alloy. The 2θ peak shift values are listed in Table 4-3. The overlap of the Fe and Fe(Al) peaks made the Fe peaks appear to be broader, Figure 4-12 and Figure 4-13.

<table>
<thead>
<tr>
<th>2θ (°)</th>
<th>Fe</th>
<th>FeAl</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg-3%Al</td>
<td>-0.076-0.128</td>
<td>+0.003-0.005</td>
</tr>
<tr>
<td>Mg-6%Al</td>
<td>-0.257</td>
<td>-0.214</td>
</tr>
</tbody>
</table>

Figure 4-14. XRD pattern of intermetallic formed on H13 steel samples dipped into 12%Al-Mg alloy

Table 4-3. The strongest 2θ peak shifts for Fe and FeAl peaks obtained after dipping into the Mg-3%Al and Mg-6%Al alloys
4.4 Mg-Al-Mn alloys dipping tests

A continuous intermetallic layer was formed on all samples dipped into the group 2 alloys, which were alloyed with 3% aluminium and 0.178wt.% to 0.56wt.% manganese.

4.4.1 Intermetallic layer morphology

Samples dipped into alloy #4 formed a continuous layer from the 5 minutes to 180 minutes of dipping time.

On samples dipped into the Mg-3%Al-0.178%Mn alloy, the intermetallic layers were continuous and their thickness could be measured on SEM images, as shown in Figure 4-15. The main observation on the 5-minute dipping sample was that the intermetallic particles were generally joined together, but some small gaps were present. On samples dipped for more than 30 minutes, a dense and continuous intermetallic layer formed. From the cross-sectioned images it was apparent that the surfaces were rough and two intermetallic layers were observed, especially for the 180 minutes dipping sample, as shown in Figure 4-15g.

On samples dipped into the Mg-3%Al-0.362%Mn alloy, the formation of intermetallic started with particles (Figure 4-16a) which were surrounded by another thin intermetallic layer (Figure 4-16d). The intermetallic formed a continuous layer across most of the sample surface area. Compared with the intermetallic appearance formed in the Mg-3%Al-0.178%Mn alloy, the intermetallic with this alloy is smoother and the intermetallic grains are denser and smaller, Figure 4-16. The intermetallic layer, however, seems to be not well bonded to the substrate as it was observed to be separating from it (Figure 4-16b, c).
Figure 4-15. Intermetallic phases on H13 steel samples dipped into Mg-3%Al-0.178%Mn alloy (Alloy #4). Images a), c), e), and g) are cross sections of samples dipped for 5, 30, 60 and 180 minutes respectively. b), d), f) and h) are their surface morphologies.
Figure 4-16. Intermetallic phases on H13 steel samples dipped into Mg-3%Al-0.362%Mn alloy (Alloy #5). a), b) and c) are cross sections of samples dipped for 5 minutes, 180 and 360 minutes respectively. d), e) and f) are corresponding surface morphology.

In the case of Alloy #6, the intermetallic layer formed quickly and the grains became uniform. The two-layer structure of this intermetallic became more distinct (Figure 4-17) with the inner layer separating from the H13 substrate.
Figure 4-17. Intermetallic appearance on H13 steel samples dipped into Mg-2.793%Al-0.52%Mn alloy (Alloy #6). a) and b) are cross sections of samples dipped for 5 and 180 minutes. c), d), e) and f) are surface morphologies of samples dipped for 5, 30, 60, 180 minutes, respectively.

The thickness of the intermetallic layer was measured from SEM image. In all cases, the continuous layer was getting smoother and its thickness increased with the increasing manganese content in the alloys. Figure 4-18 shows the intermetallic layer thickness as a function of dipping time. After 180 minutes of dipping in alloys #4, #5 and #6 which had...
0.178%, 0.362% and 0.52% manganese respectively, the correspondent thicknesses of intermetallic layers were 3.3µm, 5.4µm and 9.07µm. It was also clear that the relationship between the intermetallic layer thickness and dipping time appeared to follow a quadratic relationship. This was different from that observed with samples dipped into both the AZ91D and Group 1 Alloys.

![Figure 4-18](image)

Figure 4-18. Intermetallic layer thickness as a function of dipping time obtained from samples dipped into Group 2 alloys

### 4.4.2 Intermetallic phase identification

Intermetallic layers in the Mg-Al-Mn alloys were examined with EDX to obtain their compositions. Typical EDX spectras are shown in Figure 4-19. Figure 4-19a shows that the inner intermetallic layer was composed mainly of Al-Mn-Fe with the Fe concentration being higher than that of Mn. The EDX of the outer intermetallic layer showed similar spectra but with the Mn concentration higher than that of Fe, as shown in Figure 4-19b.
Figure 4-19. EDX spectra of intermetallic layers on the H13 surface dipped into Mg-Al-Mn alloys. a) inner layer and b) outer layer.

Table 4-4 lists all the inner and outer intermetallic layer compositions of samples dipped into Alloys #4-#6. The data were averaged from at least 5 point scans. Figure 4-20 shows the surface X-ray diffraction pattern of the samples dipped into the Mg-3%Al-Mn alloys. All dipping samples produced the FeAl (JCPDF #1-1275) phase with some Fe substituted by Mn forming the (Fe, Mn)Al phase. It was clear that with the different Mn content in the intermetallic phase, the Fe and FeAl peaks shifted which means that with the action of aluminizing of Fe and diffusing of Mn into FeAl, their crystal parameter increased. As an example, the shifted 2θ angles of the strongest <110> peaks of both Fe and FeAl are
listed in Table 4-5. it is clear that the Fe peak shift is not as severe as that of thr FeAl, which was strongly affected by the contents of Mn in the FeAl phase.

Table 4-4. Composition of intermetallic found on H13 steel samples dipped into Mg-3%Al-Mn alloys (at.%)

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Fe</th>
<th>Mn</th>
<th>Balance</th>
<th>Cr, Si, V, Mg</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Alloy Group 2</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alloy#4</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner Layer</td>
<td>44.34</td>
<td>39.41</td>
<td>15.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer Layer</td>
<td>52.49</td>
<td>19.61</td>
<td>27.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alloy#5</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner Layer</td>
<td>33.47</td>
<td>46.05</td>
<td>17.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer Layer</td>
<td>39.07</td>
<td>32.76</td>
<td>25.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>Alloy#6</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inner Layer</td>
<td>33.53</td>
<td>21.39</td>
<td>44.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Outer Layer</td>
<td>36.60</td>
<td>16.08</td>
<td>46.17</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 4-20. X-ray diffraction pattern of surfaces of the samples dipped into Mg-3%Al-Mn alloys
Table 4-5. 2-θ peak shifts for strongest Fe and FeAl peaks from samples dipped into Mg-3%Al-Mn alloys

<table>
<thead>
<tr>
<th>Alloy</th>
<th>2θ angles shifted</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>FeAl, Inner layer</td>
<td>FeAl, Outer layer</td>
</tr>
<tr>
<td>Mg-3%Al-0.178Mn</td>
<td>0.01-0.464°</td>
<td>0.32°</td>
<td>0.52°</td>
</tr>
<tr>
<td>Mg-3%Al-0.362Mn</td>
<td>0.375°</td>
<td>0.337°</td>
<td>0.63°</td>
</tr>
<tr>
<td>Mg-3%Al-0.52%Mn</td>
<td>0.16-0.41°</td>
<td>0.717°</td>
<td>0.82°</td>
</tr>
</tbody>
</table>

4.5 Summary of dipping experiments

All the dipped samples showed intermetallic phase formation at the interface of substrate and magnesium alloys. In Mg-3%Al and Mg-6%Al alloys, FeAl was the major phase with Al content varying from 51 to 53 at.%. FeAl2 was the minor phase in both alloys. Fe2Al5, according to the Fe/Al composition, was another minor phase which was not detected by XRD. Icosahedral Fe14Al86 formed when aluminium content reached 12% in magnesium alloy. In all samples dipped into Mg-3%Al-Mn alloys, only the (Fe,Mn)Al phase was detected. This was a phase in which some Fe atoms were substituted by Mn probably through the formation of intermediate phases. Fe <110> and FeAl <110> peaks in most cases were shifted because of the effect of aluminizing and the different aluminium and manganese contents in the FeAl phase.

4.6 Die casting trials

After the dipping test confirmed the possibility of intermetallic formation at the interface of H13 die steel and the magnesium alloys, a high pressure die casting trial was carried out to investigate soldering under high pressure die casting conditions. During the trial, the core pins were initially coated with a grey, thin film which is believed to be α-Mg. After about 12 shots, slight build-up was observed at the side of the core pin. The build-up material then was cleared away by the next ejection before it appeared again after 25-30 shots. Each time the build-up formed, part of the build-up layer was cleared away in the following few shots. Core pins did not experience serious soldering as in the case of aluminium high pressure die casting but all appeared to have been coated with a silvery
to dark layer with tendency of peeling off. The layer was also rougher and thicker on the area directly facing the injection gate. At the opposite side to the injection gate, the build-up was higher than on the area tangent to the injection gate. These core pins (Figure 4-21) were cut and analysed by optical and scanning electron microscopy, as well as EDX and x-ray diffraction.

![Figure 4-21. Photographs of core pins after high pressure die casting. a) core pin side facing the gate, b) core pin side 90° to a), c) core pin side opposite the gate](image)

4.6.1 Soldering morphology on the core pins

There were three important morphology features on the core pin surface after 250 shots, Figure 4-22. The dendritic magnesium build-up and drag marks formed during ejection
(Figure 4-22a, b and c). Particles with high manganese and aluminium content in magnesium matrix formed layers on the core pin surface, Figure 4-22d, e. These layers were seen broken and peeled off at some area on the core pin, Figure 4-22f.

Figure 4-22. Surface morphology of the core pin after 250 shots. a) core pin surface at the injection gate area, b) drag marks at core pin surface, c) magnesium build-up and d) Al-Mn particles, e) lower magnification of c) and d), f) layers that have broken or peeled off.
A casting was cut through the hole after the core pin was pulled out. The broken layer was detected from the core pin hole surface featuring a Al-Mn particle rich layer on top of the casting metal, Figure 4-23.

![Image of casting](image)

Figure 4-23 Surface morphology on the hole area of the casting

### 4.6.2 Intermetallic compositions and phases identification

Surface analysis of the core pins tested in high pressure die casting trials revealed that besides particles and Mg matrix build-up on the core pin surface, as shown in Figure 4-22 and Figure 4-23, there was an intermetallic phase growing from the core pin surface which, depending on the location, formed a structure consisting of an inner and an outer layer, Figure 4-24.

The insert in Figure 4-24a shows the particles on top of the intermetallic layer. The build-up and intermetallic grown from the substrate are localized, mainly in areas in front of the injection gate. More intermetallic grew from the substrate and less build-up of intermetallic particles was present in this area, Figure 4-25. With removal of the build-up intermetallic and the magnesium matrix with stannous chloride solution, the intermetallic grown from the substrate was clearly seen, Figure 4-26. It was noted that, at the gate spot, the intermetallic formed uniform layers and it was nucleated and grew along the machine marks.
Figure 4-24. Intermetallic particle build-up in the magnesium alloy matrix on a) core pin surface and b) intermetallic layers formed.
Figure 4-25. SEM images of the core pin surface in relation to the injection gate. a) the core pin schematic shows the positions of the spot 1 to 5 from front to opposite the gate in approximately 45° interval. b)-f) microstructures of areas 1-5 in a), respectively.
Figure 4-26. Intermetallic layer on the surface of core pin facing the injection gate. Some build-up particles still remained on the surface after removal of the magnesium matrix.

EDX analysis showed that the magnesium matrix on the core pin surface had a high content of aluminium. The inner intermetallic layer grown from the core pin surface had a composition in the Fe$_2$Al$_5$ range in the Al-Fe phase diagram, as shown in Table 4-6. Chromium, vanadium as well as silicon were observed in this layer.

Table 4-6. Inner and outer intermetallic compositions (at.%)

<table>
<thead>
<tr>
<th></th>
<th>Mg</th>
<th>Al</th>
<th>Mn</th>
<th>Fe</th>
<th>Others</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inner layer</td>
<td>2.79</td>
<td>74.91</td>
<td>12.17</td>
<td>9.54</td>
<td>Balance</td>
</tr>
<tr>
<td>Outer layer (Crust)</td>
<td>3.27</td>
<td>63.06</td>
<td>32.28</td>
<td>1.30</td>
<td>Balance</td>
</tr>
</tbody>
</table>

The build-up particles had higher aluminium and manganese concentration. As die casting proceeded, these particles either dissolved into the inner intermetallic layer, or segregated at the top of inner intermetallic layer and formed the outer layer with high manganese concentration. This was very similar to the inner and outer intermetallic layer formation in the dipping process. Figure 4-27 shows the EDX spectra of the inner and outer intermetallic layers found on the core pin.
XRD analysis of the core pin confirmed that both inner and outer intermetallic layers belong to the Fe$_2$Al$_5$ phase. Another peak in the XRD pattern belongs to the Mn$_5$Al$_8$ phase, as shown in Figure 4-28.

Another phase appearing on areas away from the gate spot is (FeO)$_{0.23}$(MgO)$_{0.77}$ (JCPDF #77-2366), Figure 4-29. This is the product of Fe-O reaction with magnesium. This is similar to that occurring in the dipping test, Figure 4-10.
Figure 4-28. Core pin surface XRD pattern, not etched. \( \eta \)-Orthorhombic \( \text{Fe}_2\text{Al}_5 \), \( \beta \)-Cubic \( \text{Mg}_{17}\text{Al}_{12} \)

Figure 4-29. XRD analysis of the core pin surface away from the gate spot after 200 shots showing \((\text{MgO})_x(\text{FeO})_{1-x}\) phase
4.7 Summary

All dipped samples showed intermetallic phase formation at the interface of substrate and magnesium alloys. In Mg-3%Al and Mg-6%Al alloys, FeAl was the major phase with Al content varying from 51 to 53 at.%. FeAl$_2$ was the minor phase in both alloys. Fe$_2$Al$_5$, according to the Fe/Al composition, was another minor phase which was not detected by XRD. Icosahedral Fe$_{14}$Al$_{86}$ formed when aluminium content reached 12% in magnesium alloy. In all samples dipped into the Mg-3%Al-Mn alloys, only (Fe,Mn)Al phase was detected. This was a phase in which some Fe atoms were substituted by Mn atoms. Fe $<110>$ and FeAl $<110>$ peaks in most cases were shifted because of the effect of aluminizing and the different aluminium and manganese contents in the FeAl phase.

Die casting trial showed that the Al-Fe-Mn intermetallic growth was an important but not the only soldering feature. Al-Mn intermetallic particles built-up and the MgO-FeO reaction were the other two features. These three modes happened preferentially depending on the pin positions in relation to the injection gate. Surface roughness of the pin also affected the intermetallic formation.
Chapter 5  Performance of surface coatings in preventing soldering in magnesium alloys

The surface treatment/coating technologies applied in this project involve surface oxidation, nitriding, laser cladding of Fe/W coating, PVD mono and multi layer coatings. The PVD coatings were TiN, CrN and multi layer of these in combination with nitriding. PVD and their composite coatings were also applied to H13 samples with different sample surface conditions, the as machined and 600 mesh SiC grounded. They were explained in Chapter 3.

All surface treated H13 samples were dipped into two magnesium alloys, one containing high manganese and the second high aluminium concentrations to assess their anti-soldering performance. The alloys used were Mg-12%Al and Mg-3%Al-0.5%Mn which formed intermetallic quickly and uniformly in untreated H13 dipping tests.

5.1 Performance of magnetite coating

Although the intermetallic layer, especially on the H13 sample dipped into Mg-12wt.%Al, was formed on some areas (Figure 5-1a), the main feature of the magnetite coating (JCPDF #19-0629) after dipping in both alloys was that this layer was getting thinner, from the original thickness of ~3µm to less than 1µm after dipping, Figure 3-6. A uniform top layer was formed on the magnetite coating, Figure 5-1b, c. EDX analysis, Figure 5-2, on the sample showed that magnesium was found in both the oxide coating and the top layer. The thickness of the top layer was 1-1.5µm in Mg-12%Al and 2-2.5µm in Mg-3%Al-0.5%Mn alloys and had higher magnesium content than the oxide coating, Figure 5-2. It was noted that no manganese was found in both the oxide and top layer in case of samples dipped into Mg-3%Al-0.5%Mn alloy. It was difficult to obtain accurate composition of the oxide coating by EDX because it was below 1µm in thickness.

It was observed that the oxide coating was reduced in thickness on all dipped H13 samples. From surface XRD data the new phases formed were Fe14Al86 and Fe2Al5 in the case of Mg-12%Al alloy (Figure 5-3) and Mg0.23Fe0.77O in the case of Mg-3%Al-
0.5%Mn alloys Figure 5-4. Note magnesium alloy build-up was removed with Sn\(_2\)Cl solution which left some metallic Sn deposited on the sample surface (red lines).

Figure 5-1. H13 sample with magnetite coating after dipping into magnesium alloys. a) intermetallic layer formed on part of sample dipped into Mg-12%Al, b) top layer on sample dipped into Mg-12%Al alloy, c) top layer on sample dipped into Mg-3%Al-0.5%Mn.
Figure 5-2. EDX spectra of a) the oxide coating, and b) the top layer after the sample was dipped into both Mg-12%Al and Mg-3%Al-0.5%Mn alloys for 180 minutes.

Figure 5-3. XRD pattern of the surface of the magnetite coated sample dipped into Mg-12%Al alloy for 180 minutes.
Figure 5-4 XRD pattern of the surface of the magnetite coated sample dipped into Mg-3%Al-0.5%Mn alloy for 180 minutes

5.2 Performance of nitrided coatings

The intermetallic phase on the nitrided H13 sample with grounded or un-grounded substrate before nitriding could not be clearly identified after dipping into both alloys. The sample surface became rough and it appeared that the nitride coating on the sample was dissolved into the alloy (Figure 5-5a). Magnesium content was very high in this area. Calcium from the special mounting material was detected because the x-ray spot was not small enough (Figure 5-7a).

The surface of the nitrided H13 sample dipped into the Mg-3%Al-0.5%Mn alloy showed that a small amount of Al-Fe-Mn intermetallic particles segregated on top of the surface (Figure 5-6). Point B had a higher Fe concentration which was similar to point A, and Point C has a higher Mg concentration than the other areas (Figure 5-7b, c).
X-ray diffraction of the nitrided H13 sample surface after removal of the adhering magnesium alloy showed that all the original Fe-N phases, mainly Fe₃N (JCPDF #76-91), Fe₄N (JCPDF #83-231) disappeared in both cases, but the CrN phase (JCPDF #11-65) appeared from the nitrided substrate. Though some intermetallic particles were spotted, they were not detected by the XRD (Figure 5-8). Note that the magnesium alloy build-up was removed with Sn₂Cl solution which left some Sn deposited on the sample surface (red lines).
Figure 5-7. EDX spectra.  a) At point A in Figure 5-5; b) and c) at point B and C in Figure 5-6.
Figure 5-8. XRD patterns of nitrided H13 sample surface dipped into a) Mg-12%Al and b) Mg-3%Al-0.5%Mn alloys for 180 minutes

5.3 Performance of Fe/W laser clad coating

A discontinuous intermetallic layer formed only at the Fe matrix area on samples dipped into both Mg-12%Al and Mg-3%Al-0.5%Mn alloys. There was no intermetallic formed on top of the W particles (Figure 5-9a-d). About 50% of the surface area was covered
with the intermetallic, which was equivalent to the Fe proportion in the cladding powder. EDX spectras of the intermetallic phases in both alloys were the same as those of uncoated H13 samples dipped into the same alloys (Figure 5-10). According to the EDX and previous H13 dipping experiments, the intermetallic grown from the substrate was Fe$_{14}$Al$_{86}$ in Mg-12%Al alloy and (Fe, Mn)Al in Mg-3%Al-0.5%Mn alloy.

Figure 5-9. Laser clad Fe+W coating dipped into Mg-12%Al alloy (a and b) and Mg-3%Al-0.5%Mn alloy (c and d)
Figure 5-10. EDX spectra of the intermetallic layers formed on laser clad samples dipped into a) Mg-12%Al alloy and b) Mg-3%Al-0.5%Mn alloy.

5.4 Performance of TiN PVD coating

The TiN PVD coating was prepared on two different substrate surface conditions. One side of the coupon was left as machined and the other side was slightly grounded with 600 mesh SiC paper. It can be observed in Figure 5-11 that the grounded surface was very clean after dipping into Mg-12%Al alloy, with no intermetallic. However, the ungrounded surface showed poor resistance to the melt attack with about 40% of the coated area being covered with the intermetallic growing from the substrate, Figure 5-11b, d. The intermetallic had a similar EDX spectra to that of untreated H13 sample, as shown in Figure 5-12.
In the Mg-3%Al-0.5%Mn alloy, the coating performed very well and no damage was detected on the polished and unpolished surfaces of the sample (Figure 5-13).

Figure 5-11. TiN coating performance in Mg-12%Al alloy. Cross section and surface view on (a and c) the grounded and (b and d) the as machined substrates

Figure 5-12 EDX spectra of intermetallic formed on PVD TiN coating dipped into Mg-12%Al alloy
Figure 5-13. TiN coating performance in Mg-3%Al-0.5%Mn alloy. Cross section and surface view on (a and c) the grounded and (b and d) the as machined substrates.

XRD (Figure 5-14a) of the coated samples detected $\text{Fe}_{14}\text{Al}_{86}$ (JCPDF #39-824) and $\text{Fe}_2\text{Al}_5$ (JCPDF #47-1435) phases on the coated H13 sample dipped into the Mg-12%Al alloy. The sample dipped into the Mg-3%Al-0.5%Mn produced a similar XRD pattern apart from the stronger Fe peak indicating that the TiN (JCPDF #87-633) coating was getting thinner, Figure 5-14b. Note that the magnesium alloy build-up was removed with Sn$_2$Cl solution which left a small amount of Sn deposited on the sample surface (red lines).
Figure 5-14. XRD of pattern of TiN coated samples dipped into a) Mg-12%Al and b) Mg-3%Al-0.5%Mn alloys for 180 minutes
5.5 Performance of CrN PVD coating

The CrN coating in the Mg-12%Al alloy showed very different soldering resistance. On the grounded side, a reaction layer formed on top of the CrN coating and this made the CrN coating thinner, Figure 5-15a. Also, aluminium was found in this layer, Figure 5-16a. The reacted layer contained higher aluminium content and only a very small amount of Cr, Figure 5-16b. This layer covered over 50% of the total sample surface. On the other side, where the substrate was in as machined condition before coating, the intermetallic compound formed nearly all over the sample surface Figure 5-15b. This layer had a similar EDX spectra as the untreated H13 tool steel sample dipped into the same alloy. This reaction rarely occurred on the grounded side.

Figure 5-15. CrN coated samples dipped into Mg-12%Al alloy. a) grounded substrate, b) as machined substrate
Figure 5-16. EDX of CrN coating dipped into Mg-12%Al alloy. a) the CrN coating, b) the reacted layer on top of CrN coating and c) intermetallic layer
The CrN coating in the Mg-3%Al-0.5%Mn did not show much difference on grounded and as machined sides of the sample. All samples had intermetallic particles attached to them and at some areas these particles soldered to the H13 substrate forming the penetration area Figure 5-17a, and b. The intermetallic particles have an Al, Mn, Cr and Fe composition (Figure 5-18a) and the original coating between particle and the substrate seemed to disappear while Al and Mg appeared to be the major elements present, Figure 5-18b.

Figure 5-17. CrN coated samples dipped into Mg-3%Al-0.5%Mn alloy. a) Intermetallic particles on the coated surface. b) Intermetallic penetrated the CrN coating. c) and d) CrN coating surface on grounded and as machine substrate, respectively
Figure 5-18. EDX spectra of intermetallic formed on CrN coating dipped into Mg-3%Al-0.5%Mn alloy. a) intermetallic particles, b) CrN coating after dipping

XRD detected Fe$_{14}$Al$_{86}$ (JCPDF #39-824) and Fe$_2$Al$_5$ (JCPDF #47-1435) phases from CrN coated H13 sample dipped into the Mg-12%Al alloy, Figure 5-19a. On coated H13 sample dipped into the Mg-3%Al-0.5%Mn, other than the CrN (JCPDF #11-65) and Cr$_2$N (JCPDF #27-127) phases, three peaks at d=2.7184, 2.035, 1.8606 could not be identified (X-phase), Figure 5-19b. The strongest peak at d=2.035 was very similar to the (Fe,Mn)Al phase which was present in uncoated H13 sample dipped into the same alloy and this peak could belong to the intermetallic particles formed on the CrN surface. Note that the magnesium alloy build-up on the sample was removed with Sn$_2$Cl solution which left some Sn deposited on the substrate surface (red lines).
Figure 5-19. XRD pattern of the CrN coated H13 samples dipped into a) Mg-12%Al and b) Mg-3%Al-0.5%Mn alloys for 180 minutes.
5.6 Performance of TiN/Nitride coating

This duplex coating was unable to protect the substrate from soldering when dipped in the Mg-12%Al alloy, regardless of the substrate’s surface preparation. Coating failed on 42-46% of the surface area with the coating peeling off or breaking away, Figure 5-20. In the Mg-3%Al-0.5%Mn alloy, this area increased to over 53% on the grounded side and over 75% on the un-grounded side, Figure 5-21. In all areas, the white layer was broken underneath the TiN coating and the intermetallic started to form, Figure 5-21b.

![Figure 5-20. TiN/Nitride coating performance in Mg-12%Al alloy after 180 minutes of dipping. a) cross-section of duplex coatings on grounded substrate and b) on the as machined substrate. c) and d) corresponding surface views. Dark areas show failed coating.](image)
Figure 5-21. TiN/Nitride coating performance in Mg-3%Al-0.5%Mn alloy after 180 minutes of dipping. a) cross-section of duplex coatings on grounded and b) on the as machined substrate. c) and d) corresponding surface views. Dark areas show failed coating.

The XRD did not detect any Al-intermetallic in samples dipped in both alloys, Figure 5-22. XRD patterns were very similar to those of nitrided samples other than the TiN peaks. After dipping, the iron peak became stronger compared to that before dipping indicate the exposing of the substrate. Note that the magnesium alloy build-up was removed with Sn₂Cl solution and left some Sn deposited on the surface (red lines).
Figure 5-22. XRD pattern of the surface of TiN/Nitride samples after dipping. a) in Mg-12%Al, and b) in Mg-3%Al-0.5%Mn alloys for 180 minutes.
5.7 Performance of CrN/Nitride coating

Two major failure features of this duplex coating system were identified after dipped into both the Mg-12%Al and Mg-3%Al-0.5%Mn alloys. Firstly, the coatings peeled off on both grounded and un-grounded substrates, Figure 5-23a and Figure 5-24a. Secondly a reaction layer formed on top of the inner layer, Figure 5-23b and Figure 5-24b. Originally this was the CrN coating. Inner and outer layers in both alloys have different EDX spectras, as shown in Figure 5-25 and Figure 5-26. The difference comes from the content of chromium and iron as well as nitrogen. The outer layers obtained from dipping into both alloys showed similar spectra, both had high Al and Cr contents. The total thickness of two layers was also similar, about 5μm. The intermetallic could be seen at locations where the coating peeled off, Figure 5-24a and Figure 5-26c. The intermetallic had similar spectra as the uncoated H13 samples dipped into the same alloy.

![Peeling off](image1)
![Reaction layer](image2)

Figure 5-23. Performance of the CrN/nitride coating in Mg-12%Al after 180 minutes of dipping. a) cross-section of coating on the grounded and b) on the as machined substrate, c) and d) are the corresponding surface views
Figure 5-24. Performance of the CrN/Nitride coating in Mg-3%Al-0.5%Mn alloy after 180 minutes of dipping. a) cross-section of coating on the grounded and b) on the as machined substrate, c) and d) are the corresponding surface views.
Figure 5-25. EDX spectra of CrN/Nitride sample after dipping into 12%Al-Mg alloy after 180 minutes of dipping. a) CrN coating, b) reaction layer
Figure 5-26. EDX spectra of CrN/Nitride coating dipped into Mg-3%Al-0.5%Mn alloy for 180 minutes. a) CrN coating, b) reaction layer and c) intermetallic layer shown in Figure 5-24a.
Similar to the CrN dipped into the Mg-12%Al alloy, the XRD detected small amount of Fe$_2$Al$_5$ phase (JCPDF #47-1435), Figure 5-27. No intermetallic phase was detected from the sample dipped into the Mg-3%Al-0.5%Mn alloy, Figure 5-28. Note that the magnesium alloy build-up was removed with Sn$_2$Cl$_2$ solution which left some Sn deposited (red lines).

Figure 5-27 XRD pattern of the surface of CrN/Nitride coating dipped into Mg-12%Al for 180 minutes
Figure 5-28. XRD pattern of the surface of CrN/Nitride coating dipped into Mg-3%Al-0.5%Mn alloys for 180 minutes

5.8 Performance of CrN/TiN/Nitride coating

This coating system showed very poor bonding to both the grounded and as machined substrate in both alloys. The coating had poor performance and peeling off was the major failure feature, as shown in Figure 5-29 and Figure 5-30. Similar to the CrN and CrN/Nitride coatings, the outer layer is composed of Mg, Al and Cr as the major elements, Figure 5-31. The intermetallic, mainly Al-Mn-Fe, was growing on the substrate on samples dipped into the Mg-3%Al-0.5%Mn alloy, very similar to the case of uncoated dipping samples.

The XRD pattern showed very small amount of the Fe$_2$Al$_3$ (JCPDF #47-1435) phase from the sample dipped into the Mg-12%Al alloy, Figure 5-32. Similar to the CrN dipping sample, very weak X-phase was observed (as arrowed) from the sample dipped into the Mg-3%Al-0.5%Mn alloy, Figure 5-33. Note that the magnesium alloy build-up was removed with Sn$_2$Cl solution which left some Sn deposited (red lines).
Figure 5-29. CrN/TiN/Nitride coating dipped into 12% Al-Mg alloy for 180 minutes. a) cross-section of coating on the grounded a) and on the as machined b) substrates, c) and d) are the corresponding surface views
Figure 5-30. CrN/TiN/Nitride coating dipped into 3%Al-0.5%Mn-Mg alloy for 180 minutes. a) cross-section of the coating on grounded a) and on the as machined b) substrates, c) and d) are the surface views.

Figure 5-31 EDX spectra of the outer layer on CrN/TiN/Nitride coating dipped into 3%Al-0.5%Mn-Mg alloy for 180 minutes.
Figure 5-32 XRD pattern of the surface of CrN/TiN/Nitride coating dipped into Mg-12%Al alloy for 180 minutes

Figure 5-33. XRD pattern of the surface of CrN/TiN/Nitride coating dipped into Mg-3%Al-0.5%Mn alloy for 180 minutes
5.9 Performance of duplex TiN/CrN coating

The duplex coating of TiN/CrN showed no reaction after dipping into the Mg-12wt%Al and Mg-3wt%Al-0.52wt%Mn alloys, regardless of the substrate surface preparation, Figure 5-34 and Figure 5-35. After 180 minutes of dipping, only few defect spots were observed and no intermetallic grew inward, but a line scan showed that there was interdiffusion of aluminium and titanium, Figure 5-36. No intermetallic phase was detected with XRD from coated H13 samples dipped into the Mg-12%Al and Mg-3wt%Al-0.52wt%Mn alloys, Figure 5-37. Note that the magnesium alloy build-up was removed with Sn₂Cl solution which left some Sn deposited on the substrate surface (red lines).

![Cross-sections of duplex coating TiN/CrN dipped into 12%Al-Mg alloy.](image)

Figure 5-34. Cross-sections of duplex coating TiN/CrN dipped into 12%Al-Mg alloy. a) cross section of coating on the grounded and b) on the as machined substrates. c) and d) are the corresponding surface views.
Figure 5-35. Duplex TiN/CrN coating on a) the grounded and b) on the as machined substrate dipped into 3%Al-0.5%Mn-Mg alloy. c) and d) are the corresponding surfaces views.

Figure 5-36 EDX line scan shows very limited inter diffusion in TiN/CrN duplex coating dipped into 3%Al-0.5%Mn-Mg alloy.
Figure 5-37. XRD pattern of the surface of duplex TiN/CrN coating samples dipped into
a) Mg-12%Al and b) Mg-3%Al-0.5%Mn alloys for 180 minutes
5.10 Summary

The experiments revealed that it is difficult to simply evaluate the performance of each coating in reducing soldering. All the coatings reduced the formation of intermetallic in different degrees. Nevertheless, it is obvious that the TiN on polished substrate and duplex TiN/CrN coating with CrN next to the substrate performed the best. With these coatings after three hours of dipping, there was no intermetallic formed on the surfaces of both coating and substrate. Intermetallic, however, was found on the CrN, nitride, laser clad and oxide coatings after dipping.
Chapter 6  Discussion

6.1  Introduction

As intermetallic formation is the major reason for soldering and associated die and casting damage, this discussion will focus on both its formation in dipping experiments and die casting trials, as well as its prevention using surface engineering approach.

From the experimental work, the H13 samples dipped into commercial AZ91D alloy and two groups of magnesium alloys (Mg-Al and Mg-Al-Mn) showed different intermetallic formation characteristics. A continuous intermetallic layer formed in all manganese containing alloys and the Mg-12wt.%Al alloy. In contrast to this, continuous intermetallic layer did not form in the Mg-3%Al and Mg-6%Al alloys. Intermetallic particles and pits or grooves on substrate surface were the main features observed, Figure 4-5 and Figure 4-6. These results demonstrated that aluminium and manganese are the two elements causing soldering and that they played different roles in the formation of intermetallic phases. Therefore, the first stage in understanding of the soldering phenomenon in magnesium alloy is to understand the roles of aluminium and manganese in the intermetallic formation.

Die casting trials demonstrated that soldering in magnesium alloys occurred and showed a different soldering mechanism to that of aluminium die casting. In addition to the intermetallic forming from the substrate, there were two other soldering features: redox reaction between iron oxide on the die surface and magnesium, and the build-up of Al-Mn intermetallic particles on top of the substrate.

All the coatings applied to solve the soldering problem resulted in better performance compared to the un-treated H13 die steel. Some coatings performed very well, resulting in no particle or intermetallic formation on the surfaces.
6.2 Intermetallic formation

6.2.1 Intermetallic formation during dipping into Mg-Al alloys

To produce a bond between two metals, one of the metals must diffuse into the other [89]. When dipping H13 samples into the Mg-Al alloys, because of the very low affinity between Fe and Mg, it was the aluminium not magnesium which diffused into the H13 substrate. It is proposed that the formation of the intermetallic alloys can be broken into several stages according to changes on the sample’s surface, as shown in Figure 6-1. At stage 1, aluminium is absorbed by the substrate. At stage 2, the inter-diffusion of Fe and Al causes formation of $\alpha$-Fe (Al). At stage 3, the nucleation of the Fe-Al phase occurs, and after this stage, there are two possibilities for the intermetallic to develop. At stage 4, where intermetallic dissolution occurs if the amount of aluminium is not high enough to maintain the stable intermetallic growth, and/or at stage 4’ where the intermetallic grows provided there is enough aluminium in the Mg-Al melt.

Figure 6-1. Schematic illustration of intermetallic formation in H13 samples dipped into Mg-Al alloys.
At the first stage, aluminium is absorbed by the substrate because of the high affinity between aluminium and iron. To form a further reaction, the system needs to possess enough energy, in the form of thermal energy (high temperature), radiation or mechanical energy to activate it [90]. In the case of H13 samples dipped into the Mg-Al alloys, the energy comes from high temperature. The ideal condition is that if the substrate surface is homogenous it will be fully covered by the aluminium, however, in practice, this surface homogeneity is hard to achieve making the absorption non-uniform and the intermetallic nucleation heterogeneous.

In the second stage, the system has reached the activation energy of the aluminizing process and overcame the interface energy barrier leading to the aluminium diffusing into the H13 steel surface and forming the $\alpha$-Fe(Al) solid solution. The reaction occurs at the grain boundaries because of the comparatively low nucleation energy barrier [38]. This phase, according to the Fe-Al phase diagram [91], may contain up to 28wt.% of aluminium. With the increased amount of aluminium in iron, the Fe crystal lattice increases and this was demonstrated by the shifted 20 peaks in the X-ray diffraction pattern, as was shown in Table 4-3, Figure 4-12 and Figure 4-13. In the Mg-3%Al alloy, the shift in the 20 angle was up to 0.127° and in the Mg-6%Al alloy this angle increased to 0.257°.

The Fe-Al intermetallic phases, mainly FeAl, formed in the third stage in the Mg-3%Al and Mg-6%Al alloys. XRD also showed shifted FeAl peaks (Table 4-3). This demonstrated that this phase had different aluminium content and was actually transformed from the $\alpha$-Fe(Al) with gradually increased aluminium content. The appearance of minor phases, FeAl$_2$ and Fe$_2$Al$_5$ (Figure 6-2) on the substrate in the Mg-6%Al alloy was also due to the same reason. It was seen that the FeAl$_2$ usually appeared in the duplex form with FeAl and Fe$_2$Al$_5$. In a similar study performed by Bastin et al.[92], they observed a duplex cellular morphology between the eutectoid and the hyper-eutectoid dendritic region.
Figure 6-2. Intermetallic particles formed during the dipping of H13 sample into Mg-6%Al alloy for 3 hours

The intermetallic particles in Figure 6-2 are well defined particles of FeAl, FeAl₂ and Fe₂Al₅. Many particles were in duplex form, like particle A which is a duplex particle of FeAl₂ and Fe₂Al₅.

The fourth stage involves a diffusion process and results in the growth of intermetallic particles and, in certain conditions, the intermetallic layer. In the Mg-3%Al and Mg-6%Al alloys, the continuous layer did not form. This is due to the fact that the intermetallic and substrate dissolution rates were higher than the intermetallic growth rate. Simultaneously, with the intermetallic growth, dissolution of substrate and intermetallic to the Mg-Al alloy melt took place. To establish an intermetallic layer on the substrate surface, its growth rate had to be higher than the dissolution rate. That is, given R to be the intermetallic growth rate on the substrate and R_form and R_diss to be the intermetallic thickness formed and dissolved respectively, R=R_form−R_diss. Then a stable intermetallic formation on the substrate surface was the result of R_form>R_diss, [93]. But in
these two alloys, $R_{\text{form}} < R_{\text{diss}}$, which led to the formation of discontinuous intermetallic particles on the substrate surface.

This was verified with SEM images, as shown in Figure 4-5. When the sample was dipped for 5 minutes in the Mg-3%Al alloy, the intermetallic phases appeared, and after 30 minutes more particles appeared and nearly covered the local area. As the dipping time reached 60 minutes, particles almost disappeared and pits started to form. Prolonged dipping time resulted in further dissolution leading to the enlargement of pits and the large material loss from the surface and formation of a groove, Figure 4-5. This demonstrated that in the whole dipping process in this alloy, the first three stages are finished within 30 minutes of commencing the test and after that, the intermetallic diffusion and dissolution plays the major role in the reaction. As dissolution of the substrate proceeded, the root of the particles was etched away and because of the lack of aluminium supply and the disappearance of the roots of intermetallic particles led to the particles floating on the substrate surface. The particles then separated from the substrate and settled to the bottom of crucible. At the same time, the badly aluminized substrate became loose and could be removed away from the base body leaving behind the pits[36]. In the case of dipping into the Mg-6%Al alloy, only the particles formed and there were no pits observed. This demonstrates that the intermetallic growth rate and dissolution rate are quite similar which means that aluminium is near the critical amount for continuous intermetallic formation. The slow formation of intermetallic agreed well with references [60], [27], [26] and [58].

The Fe-Al intermetallic reaction was also in good agreement with references [60], [27], [26] and [58] in the alloy with 12% of aluminium. In this case, the quick formation of the intermetallic layer of a quasi-crystal Fe$_{14}$Al$_{86}$ phase was due to higher aluminium content which led to higher formation rate [94]. With higher aluminium content in this alloy, there always was enough fresh aluminium to support the intermetallic formation and maintain the continuous inter-diffusion of aluminium and iron as well as the formed intermetallic. However, it is still not clear why this particular phase forms rather than other Fe-Al phases, like Fe$_2$Al$_5$, the most preferably grown in the Fe-Al system, [39,59,90,93,95,96]. The metastable environment supplied by the magnesium and the
reasonably quick cooling rate [97-101] after removing the sample from the melt may favour the formation of this phase.

6.2.2 Intermetallic formation when dipping into Mg-3%Al-Mn alloys

The intermetallic layer on the H13 surface dipped into Mg-3%Al-Mn alloys formed easily in all three different alloys, and its thickness was detectable, even after dipping for 5 minutes. Another observed difference from the H13 samples dipped into the Mg-Al alloys was the two-layered intermetallic structure, with the outer layer higher in manganese and the inner higher in iron content as shown schematically in Figure 6-3.

Figure 6-3. Intermetallic layer formation in the dipping of H13 sample into Mg-3%Al-Mn alloys

The first stage of the intermetallic formation was similar to that in the Mg-Al alloys, but the diffusion of aluminium toward the substrate was accompanied with the diffusion of Mn, in the form of Mn-Al intermetallic. In the second stage, the reactions between Fe and Al as well as Fe with Mn-Al happened to nucleate Fe-Al intermetallic in the ternary form of (Fe, Mn)-Al. Because the intermetallic formation on the substrate surface accompanied metastable phase MnAl deposition, the intermetallic layer formed faster than in the Mg-
Al alloy with aluminium contents lower than 7%. In all dipping tests into the Mg-3%Al-Mn alloys, the (Fe, Mn)Al was the phase that formed independent of manganese content in the melt.

The H13 sample surface dipped into the Mg-3%Al-0.362%Mn for 5 minutes is shown in Figure 6-4. The intermetallic particles identified as (Fe, Mn)Al seemed to be spread all over the surface. These particles were surrounded by a light colored, very thin intermetallic layer. It is clear from this image that after only dipping for 5 minutes, the intermetallic reaction reached the second stage.

In the third stage, the formed intermetallic particles grew to form an inner intermetallic layer. Simultaneously, very thin light colored layer continued to grow and cover the particles - resulting in the inner layer - and eventually forming the outer layer, a shell like layer.

The last stage in this reaction, as was mentioned before, was the growth of FeAl and the replacement of Fe by Mn. In commercial magnesium alloys, especially low aluminium magnesium alloys containing manganese, MnAl is a major phase which is metastable and has different crystal structure and/or parameters, for example tetragonal and hexagonal [57,59,60,102-104]. It is possible that when certain number of Mn atoms were substituted by Fe, this metastable phase was stabilised and changed to the cubic (Fe, Mn)Al crystal structure. Since a large amount of Mn was present in this phase, 2θ angles of this phase shifted considerably, Figure 4-5.

From this analysis, it is clear that the inner intermetallic layer was formed from the substrate in the first stage and grew because of the further diffusion. The outer layer was possibly formed by the deposition of the Al-Mn intermetallic particles. In this case, at the initial stage, the intermetallic layer formed rather quickly. After this, further inward diffusion of Mn and Al increased the thickness of the intermetallic, but the outward diffusion of Fe was stopped at the outer layer because of the substitution action. Therefore, another outer layer’s property is to protect the magnesium melt from being contaminated by Fe [94,105].
Figure 6-4. H13 samples dipped into Mg-3%Al-0.362%Mn alloy (Alloy #5) for 5 minutes.

Shown in Figure 6-5 is the comparison of the proposed intermetallic formation mechanism (on the left hand side) with the final intermetallic surface (on the right hand side). It is clear that both are compatible with the previous intermetallic shown in Figure 4-16.
Figure 6-5. Schematic illustration of the intermetallic layers formed when dipping into Mg-3%Al-Mn alloys. a) Schematic sample section and b) in Mg-3%Al-0.362%Mn for 6 hours. (white flakes on top of the intermetallic are Sn deposits from the reaction between Mg and etchant)

6.2.3 Intermetallic formation in high pressure die casting trial

As mentioned in Chapter 4, the Fe-Mn-Al intermetallic growing on the core pin and Al-Mn (mainly of Mn₅Al₈ in commercial magnesium alloys) build-up in the Mg alloy matrix caused soldering. The thin (MgO)ₓ(FeO)₁₋ₓ layer was another possibility for initiating soldering. Usually, soldering is a result of dual or triple co-existing reactions [105]. Therefore these three modes represented all soldering phenomenon in magnesium high pressure die casting.

The formation of each mode is discussed in detail below.

6.2.3.1 Formation of (MgO)ₓ(FeO)₁₋ₓ

It is common that the die surface is usually covered with a layer of dark iron oxide (Fe₃O₄) because of exposure to atmosphere at high temperatures. This layer when in
contact with magnesium under certain temperature will cause a redox reaction [106]. Magnesium reduces the iron oxide with the following reactions,

\[ \text{Fe}_3\text{O}_4 + 4\text{Mg} \rightarrow 3\text{Fe} + 4\text{MgO} \]  

(1)

Or

\[ \text{Fe}_3\text{O}_4 + 4\text{Mg} \rightarrow (\text{FeO})_x(\text{MgO})_y \]  

(2)

The iron from reaction (1) can then either react with Al to form the Fe-Al intermetallic or substitute Mn in the Al-Mn built-up layer and make the built-up layer grow faster. The \((\text{FeO})_x(\text{MgO})_y\) will remain in the build-up layer and form a soldering layer if the redox reaction is not completed.

At the core pin surface opposite the injection gate, the redox produced layer will remain on the core pin surface until it is fully dissolved by magnesium.

6.2.3.2 Formation Al-Fe-Mn from the substrate

If the redox reaction is completed, Fe will react with Al and form the Fe-Al intermetallic easily. The intermetallic formed may either be added to the substrate surface to stimulate further intermetallic growth or be separated from the surface together with MgO. If the redox reaction is not complete, the \((\text{FeO})_x(\text{MgO})_y\) phase forms a thin layer and stays on the surface. At locations facing or near the injection impingement spot, this layer is removed by the injecting magnesium alloy together with some Al-Mn intermetallic precipitated particles. With the effect of abrasion, the fresh die surface appears and will react with the alloy melt which is still at high temperature, Figure 3-6. The \((\text{FeO})_x(\text{MgO})_y\) layer at the areas facing the injection gate is more likely to be removed, therefore, the molten magnesium alloy will meet fresh die surface leading to the intermetallic reactions as occurred in the dipping tests and the intermetallic in these areas nucleates and grows faster, as was shown in Fig 4-25. On the side of the core pin opposite the injection gate, the \((\text{FeO})_x(\text{MgO})_y\) layer was still present on the core pin surface.
Other than the intermetallic locations corresponding to the injection spot, another feature of the intermetallic formation was that the intermetallic started to form along the machine marks, as shown in Figure 6-6. This is because at the machine mark, either oxide layer or its reaction products, (MgO)_x(FeO)_y, can be removed by injection erosion and expose the fresh die surface leading to the reaction priority. It is also because at the edge or a sharp tip of a certain shape like the machine mark, its nucleation energy barrier is easier to be overcome or it is easy to absorb energy at these places, leading to a preferred nucleation site [38].

The machine marks left on the core pin surface, on the other hand, also showed that the erosion effect because of the injection impingement is limited to the surface oxide layer or its reaction product. No erosion of the core pin surface was observed. This is in good agreement with Chen’s study on the die erosion during high pressure die casting of aluminium alloys [31].

The intermetallic reaction between Fe and Al resulted the Fe₂Al₅ Or (Fe, Mn)₂Al₅ phase. This phase is reported as the major Fe-Al phase in commercial AZ91D alloy with part of Fe atoms substituted by Mn atoms [57,59,107]. Compared with phases formed when dipping into different Mg-Al alloys in the Fe₂Al₅ began to appear when aluminium content reached 6wt%. This is in good agreement with Mukhina et al.’s result which was 4.9wt.%Al when this phase was observed in magnesium alloys [57]. Therefore, it is easy to conclude that the aluminium content is the decisive factor for forming different Fe-Al phases. The quick formation of (Fe, Mn)₂Al₅ also demonstrated that the intermetallic formation on the die surface can be linked with Fe solubility, with higher than 7% aluminium in magnesium alloys, this value increased abruptly and led to the preferred formation of this phase [60].

Fe₂Al₅ grows preferentially and becomes the major phase in most iron aluminium reactions in aluminium [47,93,106,108-110] and magnesium [57,59] alloys because as mentioned by Ryabov [90] it has the highest diffusion coefficient. Also, its crystallographic defects, where a large number of aluminium vacancies exist along the c-axis of its orthorhombic cell structure, allows greater diffusion along this axis [90,96].
In the high pressure die casting process, as soon as the fresh substrate surface is subjected to the impingement of AZ91D magnesium alloy, the Fe-Al intermetallic reaction occurs because of the strong affinity between these two elements at the comparatively high temperature rather than with magnesium, Figure 3-5. According to the Mg-Al phase diagram [64], for AZ91D in the temperature range from 437-595°C, the magnesium solid solution grows from the liquid and makes the liquid enriched in aluminium. Furthermore, this temperature makes the magnesium a semisolid and thus the ‘Alumina Gradient Effect’ (Section 2-4-2) leads to high aluminium content at the die/casting interface causing quick formation of $\beta$-Mg$_{17}$Al$_{12}$ and nucleation of the Fe-Al intermetallic.

### 6.2.3.3 The build-up of the Mn-Al particles

The intermetallic particles of Mn-Al were found to be Mn$_5$Al$_3$, Section 4.6 (Figure 4-25 to Figure 4-28). These particles precipitated from AZ91D at the temperature over 670°C.
and are quite stable. During die casting, these particles form from the alloy in the crucible which was kept at around 680°C with further precipitation in the shot sleeve. During solidification of the casting, these particles attached to the die surface accompanied with aluminium. Because of the high affinity of aluminium for iron and the above mentioned ‘Alumina Gradient Effect’, the casting alloy in the vicinity of the die had high aluminium content [6]. Thus there was a thin layer rich in aluminium and aluminium-manganese particles left on the die surface after each casting. Part of this layer can be removed by the following cast cycle but as the casting process proceeds, more and more particles remain on the surface forming a thick layer, up to 50-60μm.

Mn₅Al₈ particle build-up can be seen on the core pin surface after 15 shots. Figure 6-7 showed their appearance after 250 shots after the magnesium alloy was removed by the etchant. It was found in this experiment that 13at.% of Fe was soluble in this phase, much higher than that found by Byun et al.[111]. This may be attributed to the direct contact of the magnesium alloy with die steel. It seems that as soon as the build-up layer was formed, the Mn₅Al₈ particles grew with the die casting process, with large facet of the particles nearly parallel to the substrate surface (Figure 4-24a). They gradually developed into a layer on top of the Fe₂Al₅ intermetallic grown from the substrate, Figure 4-24b and Figure 4-25c. From this point of view, the growth of the outer layer is a result of the solid state reaction.
Figure 6-7. Appearance of the intermetallic on the core pin after 250 shots. Both Fe$_2$Al$_5$ and Mn$_5$Al$_8$ phases were identified.

Unlike the (Fe, Mn)$_2$Al$_5$ grown from the substrate, soldering caused by the Al-Mn intermetallic build-up does not harm the substrate directly, but it will badly degrade the quality of casting surface. From the fact that Fe can be dissolved into this phase, it can be concluded that this phase can reduce the amount of iron diffusing outward so that it may protect the magnesium alloy from contamination. On the other hand, aluminium diffusing inward through this layer then results in comparatively high aluminium content on the substrate surface which helps nucleation and growth of the Fe-Al intermetallic. Further, diffusion of aluminium through this layer helps the growth of the inner Fe-Al intermetallic layer. So the build-up of Mn$_5$Al$_8$ is more harmful to the whole high pressure magnesium die casting process because of damage to the die, the shot sleeve and degradation of the casting. This has been proven in industrial production [16, 61].
6.2.4 Kinetics of intermetallic formation

Intermetallic thickness as a function of reaction time is typically described by the following equation [43,47,109,112]:

\[ Y = k t^n \] (3)

or

\[ R_g = n k t^{n-1} \] (4)

where \( Y \) is the intermetallic thickness, \( R_g \) is the growth rate, \( k \) is the growth rate constant, \( t \) is the reaction time and \( n \) is the time component. If \( n = 0.5 \), the reaction is diffusion controlled and the \( Y-t \) relationship is quadratic. If \( n = 1 \), the reaction is surface controlled and the \( Y-t \) relationship is linear. As shown in Chapter 4, the intermetallic follows a linear growth mode in AZ91D, and quadratic in Mn-3%Al-Mn alloys. In the Mg-12%Al alloy, at 3 hours of dipping time, the intermetallic growth mode transforms from the linear to quadratic.

It was not clear why the Fe\textsubscript{14}Al\textsubscript{86} follows the linear growth mode for the first 3 hours of dipping into the Mg-12wt.%Al. There was no similarity between the conditions of this experiment to those where such phases were originally found [99,100,113-116], involving very high cooling rates. One thing, however, is common between these studies, such a phase can be regarded as metastable and quasi-crystalline because its icosahedral structure is quasi-periodic in two dimensions and periodic in the third [101]. In this study, the comparatively high aluminium diffusion towards the substrate surface than counter the diffusion of iron, made the intermetallic structure contain high aluminium. When cooling the sample, this aluminium may be frozen in it forming this quasi-crystal structure. So the linear intermetallic growth mode may be due to its metastable crystallographic properties and the direct contact of Fe with the magnesium melt containing high aluminium content. Fortunately, this situation is unlikely to occur in high pressure die casting of magnesium alloy. In AZ91D, as previously mentioned, the formation of the outer Mn rich intermetallic layer may reduce the outward diffusion of Fe.
and protect the intermetallic from dissolution. Also, this layer does not have much effect on the inward diffusion of aluminium. Together with the substitution of Fe by Mn, all these factors helped the total intermetallic thickness grow at a constant linear growth rate. Therefore, the intermetallic growth mode at the interface of die steel and magnesium alloys is regarded as diffusion dominated. From this point of view, the equation (3) may not be suitable to fully describe the reactions occurring in such systems.

Thus the growth rate constant, k, in equation (3), can be written as ([37,112,117])

$$k = A \exp\left(\frac{-E_A}{RT}\right)$$  \hspace{1cm} (4)

Thus

$$R_g = n A \exp\left(\frac{-E_A}{RT}\right)t^{n-1}$$  \hspace{1cm} (5)

Where $E_A$ is the reaction activation energy, J mol$^{-1}$, $R$, the gas constant, J K$^{-1}$ mol$^{-1}$, and $T$, the temperature, K.

The major difference compared with reactions in aluminium alloys is the value of the constant $A$, or the frequency factor. Also, the number of sites per unit volume at which intermetallic nucleation embryos can form, the number of atoms in the matrix at the surface of the critical embryo, the vibration frequency of these atoms and the probability that attachment of the atoms may only occur preferentially at certain points on the embryo’s surface. In magnesium alloys, as $A$ is much smaller because of the lower aluminium content and comparatively higher dissolution rate, the intermetallic growth rate is greatly reduced.

### 6.2.5 Roles of aluminium and manganese in intermetallic formation

#### 6.2.5.1 Phases governed by Al content

From the results and above discussion, it is clear that the intermetallic phases formed on the substrate surface (dipping and die casting) were governed by the content of
aluminium in the melt. When the aluminium content in the melt is lower than about 6wt.%, the FeAl and FeAl2 were formed and traces of Fe2Al5 could be detected, regardless of the amount of manganese in the alloys. This agrees well with the results of Haitani [58]. The Fe2Al5 is the major intermetallic phase formed in the magnesium alloys containing 8-9% aluminium, as in the AZ91D. This agrees well with Lashko et al. [59] and Mukhina et al. [57]. The intermetallic formed during dipping into magnesium alloy with 12% aluminium was characterized Fe14Al86 with the aluminium ranging from 79% in the outer particles to 86% in the layer next to substrate, Section 4.3.2. Table 6-1 summarises the intermetallic phases present as a function of Al content in the melt.

Table 6-1. Relationship between intermetallic type and aluminium content in magnesium alloys

<table>
<thead>
<tr>
<th>Aluminium content, wt%</th>
<th>3</th>
<th>6</th>
<th>9</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>Intermetallic phase</td>
<td>FeAl</td>
<td>FeAl, FeAl2, Fe2Al5</td>
<td>Fe2Al5</td>
<td>Fe14Al86</td>
</tr>
</tbody>
</table>

6.2.5.2 Mn effects

Manganese did not change the intermetallic phases grown from the substrate. Its existence in the intermetallic phases was mainly as a substitute for the iron atoms. This is in good agreement with other researchers [57,59]. Mn-Al phases formed in the magnesium alloys have dual roles in the soldering reactions. On one hand, they helped form the outer intermetallic layer by the deposition effect. After this layer was formed, it helped reduce the diffusion of Fe outward to the molten magnesium alloy and therefore protected the alloy from Fe contamination. On the other hand, this outer layer was a major soldering phenomenon in high pressure die casting, and any inward aluminium diffusion was restrained within the Al-Mn layer and the substrate. This increased the local Al content and therefore helped the formation and growth of the Fe-Al intermetallic phase and reduced the Fe-Al dissolution outward to the molten alloys and increased the intermetallic thickness. This makes soldering more severe.
6.2.5.3 Shifted 2-θ angles

During the XRD scans of the intermetallic formed in soldering reaction, it was found that the major 2-θ angles were shifted from their original position indicating that the lattice parameters of the intermetallic phases were changed, Table 4-3 and Table 4-5. The composition of intermetallic phase was also changed. Figure 6-8 shows the composition of the outer intermetallic formed during dipping into the Mg-3%Al-Mn alloys as a function of dipping time. It can be seen that the composition of the stable phase (Fe, Mn)Al changes with dipping time. This means that its lattice parameter was also affected. This phase had peaks shifted from the original FeAl peaks. Smaller 2-θ angle reflects the increased crystal lattice, which was also reported by Lashko et al.[59].

![Figure 6-8](image)

Figure 6-8. Changes in the composition of the outer intermetallic layer when dipped into the Mg-3%Al-Mn alloys

Similar phenomenon occurred when dipping into the Mg-Al system. Shown in Figure 6-9 is the XRD scan across the intermetallic layer from the substrate to magnesium alloy when the sample was dipped into the Mg-12%Al alloy. It is clear that the Fe$_{14}$Al$_{86}$ intermetallic peak was shifted with aluminium content increasing from 79at.% to 86at.%. This means that the crystal lattice of Fe$_{14}$Al$_{86}$ increases with increasing aluminium content.
Figure 6-9. XRD scan across the intermetallic layer from substrate to soldered magnesium alloy. 2-θ angle shift of the Fe$_{14}$Al$_{86}$ is about 0.3°

### 6.3 Evaluation of coatings performance

From the results in Chapter 4, it is clear that by applying the various surface treatments, oxidation, nitriding and surface coatings, the amount of intermetallic formed on the substrate was reduced compared to non-treated samples. Although it is not possible to compare the coatings’ performance directly a number of observation can be made. Firstly, all the coated samples performed better than uncoated ones. Secondly, there are different failure modes, such as the intermetallic growth (oxide coating, laser cladding, TiN), the coating peeling off (all coatings on the nitrided substrate, TiN on as machined substrate), the coating dissolving (white layer of nitrided H13), and the coating cracking (TiN, TiN/Nitride, CrN/Nitride). Also, the same coating can perform differently when dipped into a different alloy. For example, the TiN on as machined substrate performed well in the Mg-3%Al-0.5%Mn alloy but failed to protect the substrate in the Mg-12%Al alloy. On the other hand, there are possibilities to improve the coating performance. For example, if more W particles can be included in the coating the laser clad samples may perform better.
The Fe₃₋₄N phases on all nitrided samples were absent after dipping. Coatings, especially the TiN, on grounded surface performed much better than the same coating on as machined substrate. Composite coating of CrN/TiN/Nitride with the TiN next to the substrate and the duplex coating of TiN/CrN with the CrN next to the substrate performed differently. The former one failed to protect the substrate and the later one showed no reaction with the alloy melt.

The effect of these surface treatment methods on reducing the formation of intermetallic is discussed in some detail below.

### 6.3.1 Oxide coating

The oxide coating, magnetite, which was successfully used to reduce soldering in aluminium high pressure die casting [23], raised the possibility of reducing soldering in magnesium die casting. As was shown in Chapter 5, Figure 5-2a, this was not the case. The oxide coating was missing from some areas and was substituted with a thick Fe-Al intermetallic phase. This was caused by a crack in the oxide coating and its peeling off leading to the exposure of the substrate to the molten magnesium alloy. Nevertheless, in areas where the coating did not peel, a layer formed on the oxide coating in most cases demonstrating that the oxide coating reacted with magnesium alloys. As a result, the thickness of the oxide coating was reduced from its original 4μm thickness to about 1μm. Though large amount of magnesium was found in the top layer, only very weak Fe-Mg-O peaks were found in the sample dipped into the Mg-12%Al alloy. The remaining of a high Mg content after etching with Sn₂Cl demonstrated that magnesium in this layer was as a compound. This demonstrated that the reduction of Fe₃O₄ by magnesium is not a one step reaction, unlike the reaction between magnesium and hematite which is a single step reaction [106]. That is,

Fe₃O₄+Mg→3FeO+MgO \hspace{1cm} (6.1)

FeO+Mg→Fe+MgO \hspace{1cm} (6.1')
The Fe produced from this reaction will react with aluminium leading to the formation of the Fe-Al intermetallic phases depending on the aluminium content in the alloy. In this case, if the Al content is too low, <3%, the reduced Fe content has little chance to form the intermetallic phase. This is the reason why only a very small amount of this phase was formed on the sample dipped into the Mg-3%Al-Mn alloy.

The performance of the oxide coating showed that this coating could protect the substrate from soldering to some degree in dipping experiments which were static. Nevertheless, the oxide coating did not show significant protective effect in high pressure die casting of magnesium alloys. Like the Mg$_x$Fe$_{1-x}$O phase which formed during dipping experiment, a similar (FeO)$_{y-x}$(MgO)$_{1-x}$ phase was detected on the core pin surface away from the injection gate. This was because the injection impingement effectively eroded this phase at the gate area. However away from the gate area, especially at the area opposite the gate, this phase remained and grew on the core pin surface.

Thermodynamically, this reaction can proceed in several different ways.

\[
\text{Fe}_x\text{O}_y+y\text{Mg} \rightarrow x\text{Fe}+y\text{MgO} \quad (6.2)
\]

\[
\text{Fe}_x\text{O}_y+(y-x)\text{Mg} \rightarrow x\text{FeO}+(y-x)\text{MgO} \quad (6.3)
\]

The calculated free formation energy of iron oxides, $\Delta G = \Delta H - T\Delta S$, according to data from Hayes[118,119], is listed in Table 6-2. It is clear that all the products on the right hand side of equations (6.2) and (6.3) have higher negative formation $\Delta G$, therefore these reactions were possible. According to the Fe-O phase diagram [120], when the die casting temperature is below 570°C, only the Fe$_2$O$_3$ should be formed. Then Fe$_2$O$_3$ is reduced by Mg producing MgO and FeO mixture on the substrate.

Table 6-2. Gibbs energy of different phases involved in the Fe-O and Mg reactions at 680°C

<table>
<thead>
<tr>
<th>Phase</th>
<th>Fe$_2$O$_3$</th>
<th>FeO</th>
<th>Fe$_3$O$_4$</th>
<th>MgO</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta G_T$ (kJ/g·mol)</td>
<td>-238</td>
<td>-201</td>
<td>-810.188</td>
<td>-498</td>
</tr>
</tbody>
</table>
6.3.2 Nitride coating

The so called white layer on top of the nitrided H13 substrate dissolved and disappeared during dipping, as can be seen from the surface morphology (Figure 5-5 and Figure 5-6) and XRD, Figure 5-8 results. According to Gulizia [25] and Walkowicz [121], this white layer was a compound coating of γ'-Fe₄N and ε-Fe₂₃N. At temperature of about 520ºC [122], the decomposition of these phases will occur, as

\[ \text{Fe}_2\text{N} \rightarrow \alpha-\text{Fe} + \text{N} \text{ (released)} \] [25]

The \( \alpha-\text{Fe} \) from this reaction forms the Fe-Al or Al-Fe-Mn intermetallic. But this layer was very thin (few micrometers) and the formation of CrN during nitriding [81] provided some protection. Thus only small amount of Al-Fe intermetallic was formed and probably dissolved into the alloy.

6.3.3 Laser clad W-Fe coating

From the fact that all the intermetallic was formed on the iron matrix rather than the tungsten surface, it was clear that tungsten did not react with either the aluminium or Al-Fe and Al-Mn intermetallic. This indicated that tungsten has a strong effect on eliminating soldering. The same result was achieved in a study of aluminium dipping and die casting applications [13,123]. The reason why tungsten has no affinity for aluminium is due to their difference in atomic size.

During dipping, the iron matrix, which was in direct contact with the molten magnesium alloys containing different aluminium and manganese content reacted as discussed previously and formed the Fe-Al and Al-Fe-Mn intermetallic. The possibility of reaction between W and Al is negligible as the clad die steel formed no intermetallic in aluminium alloys [13] which led to that intermetallic only forming on top on the Fe matrix, as shown in Figure 6-10.
Figure 6-10. Optical image of intermetallic formed on W+Fe clad coating when dipped into a) Mg-3%Al-0.5%Mn and b) Mg-12Al alloys.

6.3.4 PVD coatings

6.3.4.1 Monolayer coatings

TiN has been identified as the most effective coating for eliminating soldering in high pressure die casting of aluminium alloys [8,18,82] because of its high micro hardness (2300 HV 0.05) and comparatively low thermal expansion coefficient difference (CTE, $9 \times 10^{-6}/K$) with H13 die steel ($12 \times 10^{-6}/K$). Nevertheless, this difference is still too high to completely protect the substrate from the chemical reaction with aluminium as the intermetallic formed regularly on the TiN coating on as machined substrate Figure 5-11. Mitterer [18] pointed out that most of the PVD coatings are under tensile stress, therefore on a rough surface the TiN coating will bend and can easily crack. Even if it is not
cracked before it is heated, the heating during the dipping process might put more stress on the coating and break it. Thus direct contact of Al/Al-Mn with the substrate at the cracked areas will lead to the soldering reaction, Figure 6-11. The grounded substrate reduced the stress and protected the coating from failure and no intermetallic particle was seen on the coating’s surface, Figure 5-11 and Figure 5-13.

![Figure 6-11. Intermetallic formed at the cracked sites of the TiN coating on rough surface](image)

Compared with TiN, the CrN is more ductile, and has comparatively good mechanical properties and its CTE ($12 \times 10^{-6}/K$, [8]), is very similar to that of die steel, [79]. Nevertheless, this coating failed to protect the substrate from the formation of intermetallic. This was attributed to the macro-particle and coating defects that allow aluminium to penetrate through the macro/defect edges causing intermetallic formation, growth and peeling off of the coating from large area. The worst performance was obtained from the CrN deposited on as machined substrate dipped into the Mg-12%Al on which the Fe$_2$Al$_5$ and Fe$_{14}$Al$_{86}$ intermetallic covered almost the whole surface, and the CrN coating disappeared altogether.

On the grounded substrate, another layer was formed on top of the CrN coating containing large amount of aluminium. The uniform formation of this Al rich layer indicated that the CrN has affinity for aluminium. The layer formed was CrAlN and was rather smooth. Thus in die casting of magnesium alloys, there will be a tendency for aluminium absorption by the CrN coating, but this absorption may not be as harmful as aluminium in direct contact with the die steel because CrN is chemically less reactive with aluminium compared to the die steel.
The CrN coating performed better in the Mg-3%Al-0.5%Mn than in the Mg-12%Al alloy on both grounded and as machined substrates. The deposition of Al-Mn particles occurred on both sides and in some places the penetration occurred. It was clear that at lower aluminium content, the CrN coating would last longer and offer protection. So the performance of CrN was dependent on the aluminium content in the alloy. The penetration was also the result of macro particles/coating defects formed during deposition. As was shown in Chapter 2, these particles form loose bonds to their surroundings and in the dipping or die casting, the alloy can be easily removed leaving areas to be in direct contact with the molten alloy.

It is possible that the Al-Mn particles in contact with the CrN coating caused diffusion of Cr into the particle and changed its lattice. This phase was not identified with XRD thus was ascribed as the X-phase. It should also be noted that after dipping, CrN was nearly undetected on the rough side dipped into the Mg-12%Al and on both sides dipped into the Mg-3%Al-0.5%Mn. From the XRD (Figure 5-19) it is possible that during long time dipping CrN transformed to Cr$_2$N releasing N into the magnesium alloys. Cr$_2$N is harder than CrN [124] and has better resistance to corrosion, thus making this coating last longer.

Figure 6-12 shows schematically the effect of macro particles and thermal cracks on the formation of intermetallic. It should be noted that the growth of intermetallic from the cracks will most likely lead to the peeling off of the coating and the formation of intermetallic layer over a large area.

*Figure 6-12 Schematic illustration of intermetallic formation on the PVD monocoating.

* a) initial coating state (1-macro particle, 2,3-Crack), b) and c), intermetallic formation/growth at the cracked position, and macro particle was removed and intermetallic formed at its position.
6.3.4.2 Duplex coating system

The performance of the duplex coating system (CrN, TiN and CrN/TiN on the nitrided substrates) showed that the dissolution of the nitriding white layer is fatal to the integrity of the coating. This white layer is porous [122] and under high temperature forms a black layer beneath the PVD coating [25]. This directly caused the peeling off of the coatings. The formation of small amount of intermetallic demonstrated that the nitride coating, mainly of Fe$_a$(N), had good resistance to the formation of intermetallic in magnesium alloys. The intermetallic phase, Fe$_3$Al$_5$ was produced from the dissolved white layer and aluminium, the same as in nitrided samples. This means that the PVD coating did not perform better than the nitriding in preventing soldering therefore this coating system is not considered applicable for high pressure die casting of magnesium alloys. The removal of the white layer, however, before the PVD coating is applied, is worth considering but this may increase the coating’s cost.

6.3.4.3 CrN/TiN coating

The purpose of putting the CrN coating next to the die material is to produce well bonded TiN coating. With the CrN coating, which has a similar thermal expansion coefficient to the substrate producing good bonding with the die surface and its defects, macro particles and pits, covered with the TiN coating, good anti-soldering performance was obtained. Furthermore, the CrN coating eased the stress concentration caused by the rough die surface and thermal shock. Heating further relaxed the residual stresses during dipping. As previously discussed, the TiN coating on the grounded substrate surface performed very well. With the CrN underneath, the TiN coating was well bonded thus this system lasted the longest. From Table 6-3, this coating system was unchanged after dipping in both alloy groups, which highlights the coating’s excellent mechanical and chemical properties in relation to soldering.
6.3.5 Summary of coatings performance in High Pressure Die Casting

It is difficult to compare the coatings’ performance directly. However a number of observations can be made. Firstly, all coated samples performed much better than uncoated ones. Secondly, there are different failure modes, eg. intermetallic growth (oxide coating, laser clad, TiN), coating peeling off (all coatings on the nitrided substrate, TiN), coating dissolving (white layer on nitrided H13), and coating cracking (TiN, TiN/Nitride, CrN/Nitride). On the other hand, there is room for improving the performance of some of the coatings. For example, if more W particles could be added in the layer clad coating the clad samples may perform better.

The Fe3.4N phase on all nitrided samples was absent after dipping. Coatings, especially TiN, on grounded surface performed much better than the one on as machined substrate. The composite coating of CrN/TiN/Nitride with TiN next to substrate and duplex coating of CrN/TiN with CrN next to the substrate performed differently. The former one failed to protect the substrate and the later one showed no reaction with the alloy melt.

Table 6-3 summarized the performance of all the coatings tested. Coating performance can be evaluated in terms of the new phases appearing and initial phases disappearing. The CrN/TiN duplex coating appears to be the best for preventing soldering in high pressure die casting of magnesium alloys.
Table 6-3 Performance of coatings tested in this study by XRD

<table>
<thead>
<tr>
<th>Coating Type</th>
<th>Original Phase</th>
<th>After dipping</th>
<th>Phase disappeared (-ing)</th>
<th>New phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide coating</td>
<td>Fe(s*), Fe₂O₃ (vs)</td>
<td>Fe(s), Fe₁₄Al₈₆(s), Fe₂Al₅(w), Fe₃O₄(w)</td>
<td>Fe₃O₄</td>
<td>Fe₃O₄, Fe₁₄Al₈₆, Fe₂Al₅</td>
</tr>
<tr>
<td>Nitride</td>
<td>Fe₃N(s), Fe₄N(s), CrN(w)</td>
<td>Fe(vs), CrN(w)</td>
<td>Fe₂N, Fe₄N</td>
<td>Fe₂N, Fe₄N</td>
</tr>
<tr>
<td>TiN on Nitride</td>
<td>TiN(vs), Fe(w)</td>
<td>Fe(s), TiN(s), CrN(w)</td>
<td>Fe(s), TiN(s)</td>
<td>Fe₁₄Al₈₆, Fe₂Al₅</td>
</tr>
<tr>
<td>CrN</td>
<td>Fe(vs), CrN(s)</td>
<td>Fe(s), Fe₁₄Al₈₆(s), Fe₂Al₅(w), CrN(vw)</td>
<td>Fe(s), Cr₂N, Unidentified phase</td>
<td>CrN, Fe₁₄Al₈₆, Fe₂Al₅</td>
</tr>
<tr>
<td>CrN on Nitride</td>
<td>CrN(s, shifted), Fe₃N(s), Fe₄N(s)</td>
<td>Fe(s), CrN(w), Cr₂N(vw)</td>
<td>Fe(s), CrN(w), Cr₂N(w)</td>
<td>Fe₂N, Fe₄N</td>
</tr>
<tr>
<td>TiN/CrN on Nitride</td>
<td>TiN(vs), CrN(s), Fe₃N(s)</td>
<td>Fe(vs), TiN(w), CrN(vw), Fe₂Al₅(vw)</td>
<td>Fe(s), TiN(s), CrN(vw), Cr₂N(w)</td>
<td>Fe₂N, Fe₄N</td>
</tr>
<tr>
<td>(Ti, Cr)N composite</td>
<td>TiN(vs), Fe(s), CrN(w)</td>
<td>Fe(s), TiN(s), CrN(w)</td>
<td>Fe(w), TiN(S), CrN(w)</td>
<td>N/A</td>
</tr>
<tr>
<td>Laser Fe/W</td>
<td>Fe, W</td>
<td>Fe₁₄Al₈₆*</td>
<td>N/A</td>
<td>N/A</td>
</tr>
</tbody>
</table>

*s-strong, w-weak, v-very.
Chapter 7  Conclusions

This Chapter presents the conclusions reached after studying the formation of intermetallics in the dipping and high pressure die casting tests involving magnesium alloys and ways of eliminating soldering by surface engineering technologies.

7.1  Dipping tests

Dipping of H13 samples into AZ91D alloy showed that two major elements of magnesium alloys -manganese and aluminium- and the main tool steel element iron were involved in the formation and growth of the intermetallic phases. The intermetallic product consists of two phases: (Fe, Mn)$_2$Al$_5$, and Mn$_5$Al$_8$. The growth rate of intermetallic layers was linear with dip time. The effects of aluminium and manganese in the magnesium alloys on soldering formation are as follow:

1. With the aluminium content in magnesium alloys lower than 6%, the soldering reaction between H13 and casting alloy was dominated by dissolution rather than diffusion. This resulted in a very slow, discontinuous layer intermetallic formation on the die surface.

2. When the aluminium content reached 12%, the intermetallic grew quickly and followed a two-stage growth mode. When the intermetallic thickness reached 250μm the growth changed from a surface dominated reaction to a diffusion mode.

3. In the alloys of Mg-3%Al-Mn (Mn from 0.178% to 0.52%), the continuous intermetallic layer formed in all cases and followed a quadratic growth mode. With increased Mn content the intermetallic layer became thicker and smoother.

4. Aluminium content is the controlling factor in the formation of different phases. With the aluminium content below 6%, the FeAl/(Fe, Mn)Al is the major phase formed with only a small amount of FeAl$_2$ and Fe$_2$Al$_5$. With a
higher Al content, the major phase formed was the Fe₂Al₅ and the icosahedral Fe₁₄Al₈₆ formed when the aluminium content reached 12%.

5. In all the Mg-Al-Mn alloys studied in this project, Mn atoms act as a substitute for Fe in the Al-Fe phase. This helped the intermetallic growth but the outer, Mn rich, layer reduces the Fe atoms diffusing outward and made it possible to keep the Fe content low in the molten magnesium alloy.

7.2 High pressure die casting trial

In the high pressure die casting trial, soldering occurred and followed three different soldering modes: the intermetallic formation from the substrate, the redox reaction between magnesium and the oxide coating formed on the die steel surface during die casting, and the build-up of a thick (~ hundreds of micrometer) Al-Mn rich layer. The soldering mechanisms were as follow:

1. The formation of thin FeₓMg₁₋ₓO layer due to the reaction between Fe₃O₄ on the die surface and Mg. This is the first mode and may lead to the formation of the second soldering mode.

2. FeₓMg₁₋ₓO layer can be broken and removed by alloy injection or produce Fe because of further reduction reaction. The exposed die surface formed the Fe₂Al₅ intermetallic because of the high affinity of Al for Fe.

3. Al-Mn particles from the magnesium alloy and those precipitated during the injection as well as during solidification stayed on the die surface to form a thick build-up layer which affects casting quality. This build-up developed into an outer layer of rich Mn because of inter-diffusion. This was similar to the Mn role in the dipping experiments.

4. Intermetallic nucleation started along the machine marks, which indicated that there must be a relationship between soldering and die surface roughness. Thus the die life could be prolonged with smoother die surface finish.
5. The most severe soldering occurred on the area exposed to the injection gate. This was caused by the impingement of injection alloy accompanied with the abrasive erosion of precipitated intermetallic particles to the die surface.

### 7.3 Surface engineering approach

By applying a wide range of coatings to act as a barrier to prevent or reduce soldering, the following conclusions can be drawn.

1. All surfacing treatments, from oxide coating to laser cladding, from monolayer to multilayer PVD coatings, reduced intermetallic nucleation and growth from the H13 tool steel substrate. Some treatments can be further improved.

2. The best performance was achieved with the multilayer PVD TiN/CrN coating with no trace of intermetallic formation observed. The PVD TiN/CrN duplex coating on nitrided H13 did not show improved performance compared to the single coating of TiN on nitrided H13. The decomposition of the Fe-N white layer degraded the performance of the PVD coating.

3. TiN on the grounded H13 sample was another good performed coating, however, a lot of intermetallic formed on the as-machined substrate.

4. With CrN coatings, whether or not the substrate was grounded and nitrided, an intermetallic formed on top of the coating, and the coating itself was dissolving during dipping, especially in the high aluminium alloys. This result is different from previous studies.

5. On the nitrided H13 sample, other than reactions occurring with the ‘white layer’, only a very small amount of intermetallic formed. All PVD coatings on the nitrided substrate showed poor adhesion and peeled off from the substrate. This is attributed to the decomposition of Fe$_3$N and Fe$_4$N.
6. A significant potential to further reduce soldering exists from the laser clad Fe-W samples. Increasing the W content in the powder mix can reduce the formation of intermetallic between the Fe matrix and molten magnesium alloy.

7. As predicted, the oxide coating formed a Fe$_x$Mg$_{1-x}$O phase in high pressure die casting similar to that found in dipping tests.
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