Formation of Intermetallic Compound (IMC) in the H13-Magnesium Alloy System

by

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Abstract:

This paper documents research undertaken into the soldering of magnesium alloy high pressure die casting (HPDC). It is believed that the formation of intermetallic phases is because of the strong affinity for aluminium which exists in all magnesium alloy to iron which is the major element of all tool steel. Manganese plays an important role in this reaction. However, the mechanism of this soldering reaction, as well as phases in this process, are still unclear. Based on the dipping test and high pressure die casting (HPDC) of AZ91D experiment, this study explains the mechanism of the formation of this layer and identifies phases formed during the soldering process. Scanning Electron Microscope (SEM),), Energy Dispersive X-ray Analysis (Edax) and x-ray micro-diffraction system are used to analyze samples. Results show that the formation of intermetallic compound was started with the formation of the η-Fe_2Al_5 phase and segregation of F-phase $Mn_{23}Al_{77}$ at the near-interface area and followed by inter-diffusion with H13 steel at the solid-melt interface. With iron being substituted by manganese, the ternary Al-Fe-Mn system formed in the structure of η-Fe_2Al_5, forms intermetallic compound regarded as the soldering layer.

1. Introduction

Magnesium alloy is the lightest structural metal material and the number of magnesium applications in die casting has been increasing over the last decade. With many advantages of the magnesium alloys, the Mg-HPDC is becoming one of the most attractive and prospective industries. According to[1], magnesium alloys are not only 33% lighter than aluminium alloys, but also its manufacturing cost is comparatively low, despite the higher price of magnesium material. Perfect casting property makes it suitable for the thin/very thin wall casting with high quality surface finishing.

Unlike aluminium HPDC, in which soldering has been paid a great attention[2-10], little is known about HPDC soldering of magnesium alloys. Tang *et al.*[11] found that soldering in magnesium alloy die casting does happen with its own character. As good surface quality and thin wall strength are two distinct advantages of Mg HPDC[12-14], slight soldering may degrade magnesium casting. From this point, the study of soldering of Mg-alloy HPDC is very important.

Soldering in the aluminium HPDC is believed to be related to erosive wear, corrosive wear, dissolution of die materials, and development of intermetallic phases[6].

During the die filling and solidification processes, the casting alloy reacts with the die steel and forms complex intermetallic compounds because of the strong affinity of aluminium to iron[15]. For the magnesium alloys, though the formation of Mg-Fe intermetallic phase is impossible, the Al-Fe-Mn phases were found in the magnesium alloys [11,16-18]. The appearance of manganese in magnesium alloys greatly decreased the corrosion rate by forming the Al-Mn-Fe of Mn-Fe phases. So in magnesium alloys, the Fe-Mn-Al system was assumed to be critical on soldering formation of Mg-alloys. Both dipping and die casting tests were carried out to understand the soldering problem in Mg-alloy die casting.

2. Experimental Procedure

2.1 Materials

The materials selected for the experiments were H13 tool steel (Table 1) and AZ91D magnesium alloy (Table 2). H13 samples were machined into 25×25×2 mm^3 square shapes before heat treatment. After heat treatment, the samples were polished with #1200 SiC paper and cleaned in a supersonic bath. All the samples were drilled in one corner so that they could be held stable when immersed into the alloy melt. Table 1 gives the compositions of H13 steel. Same material is used in the die casting trial.

Cr	Si	Mo	C	Mn	V	Others	Fe
4.9	1.01	1.35	0.38	0.42	0.92	<0.4	Balance

Table 1. Compositions of H13 (wt.%)

Al	Mn	Zn	Si	Others (Cu, Ni, Fe)	Mg
8.18	0.104	0.90	0.011	<0.005	Balance

Table 2. Compositions of AZ91D Alloy (wt.%)

2.2 Dip Testing Set-up

The experiments were performed using a specially designed furnace with mild steel crucible for the melting of magnesium alloys. To prevent exothermic reactions from occurring, AZ91D ingots were cut and preheated before melting. Preheating the ingot removes moisture absorbed by them and/or by Mg oxide product (MgO) on the surface so that it is safe when ingot is melting or when charging.

A mixture of SF_6 (0.18%) and nitrogen was used as cover gas. The temperature of the melt was kept constant at 680°C. Figure 1 shows the schematic of the immersion set-up.

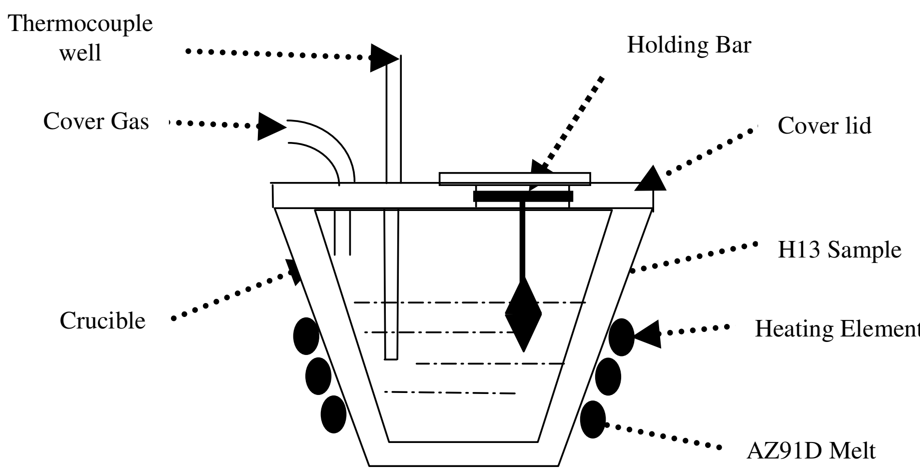


Figure 1 - Schematic Diagram of the Immersion Set-up

Samples of H13 were suspended from a holding bar into the melt for different time periods, from 5 minutes to 3 hours. Over 3/4 of each sample was immersed into the melt. To make sure that the samples contacted directly with the melt, the slag layer on the surface of the melt was scratched. To prevent the melt alloy (soldered to the sample surface) from burning, samples were covered directly by dry sand and cooled down after removal from the furnace.

2.3 HPDC of AZ91D

Set up of the HPDC of AZ91D used an accelerated die with specially positioned H13 eject pin[3]. Alloy is the same as in the dipping test. A soldering favour condition applied. The casting machine is 250DC Toshiba Die Casting Machine, located in CMST (Manufacturing Science and Technology, CSIRO) at Preston site. Alloy temperature was maintained at 680ºC. A mixture of 0.18%SF_6 + N_2 is used as cover gas. To obtain soldered castings quickly, the machine was subjected to extreme operating conditions: Injection speed: ≈80m/s, cycle time=52s, holding pressure ≈1200Kg, manual coolant spray adopted and only applied to the mild steel die.

The samples were then examined by SEM, EDS and X-ray Micro-diffraction for information on soldering layer growth rate, its composition and phase identification as well.

3. Results and discussion

3.1 Immersion test

The immersion tests indicated that the surface of H13 steel substrate was coated with some type of metallic film, as is illustrated in Figure 2. This coating appeared to be made up of a number of layers. When the surface layer was removed, another layer, "silvery" in appearance was exposed as shown on the left-hand side in Figure 2. This is the soldered layer.

Samples were cut, cold mounted and polished with great care. Under a Scanning Electron Microscope, the sectioned sample is shown in Figure 3. This not-etched metallography image clearly shows that there are three different phases in the IMC layer from identifying the different darkness labelled as phase 1, 2, and 3.

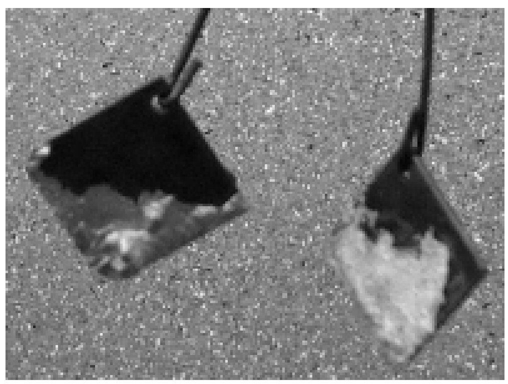


Figure2 - Example of samples after removed from the AZ91D Melt

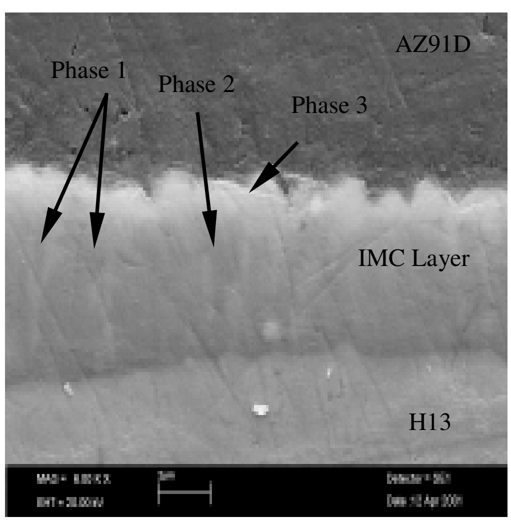
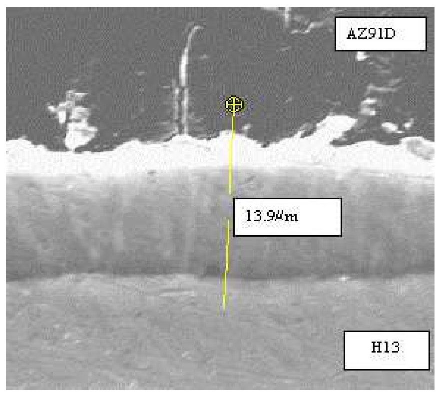


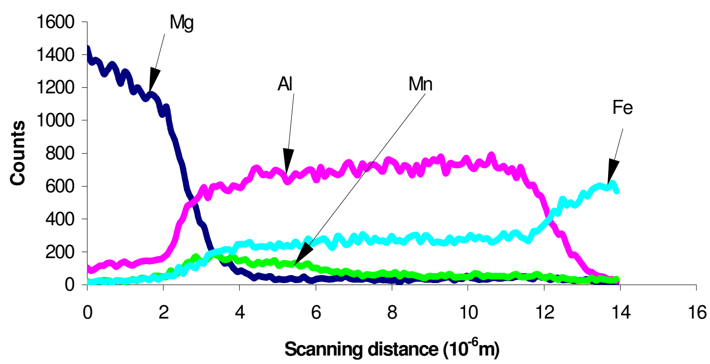
Figure 3 - SEM image of soldered area (Before etching)

(i) Phases in the intermetallic compound (IMC) layer

The major compositions of the IMC layer are iron, manganese and aluminium, as is shown in Table 3. These three elements make 98% of the atomic composition. On the contrary, magnesium, the main element in AZ91D, is neglectable. A line scan was performed using Edax, as shown in Figure 4 to show the qualitative distributions of these elements



(a)



(b)

Figure 4 Line scan of the IMC layer for the major element:
(a) Scanning correspondent image (2 hours immersion time, not etched)
(b) Major element scan result

Compared with the results for aluminium alloy soldering [19,20]this composition is nearly the same as that of orthorhombic η-Fe_2Al_5. The identification of IMC-phases using conventional X-Ray Diffraction (XRD) method is difficult because the layer is too thin and positions corresponding to certain phase can not be obtained. To overcome this difficult, the X-Ray micro-diffraction technique is adopted[21]. The sample was polished as shown in Figure 5. Point 1 and point 3 are interfaces between IMC-AZ91D and IMC-H13 respectively.

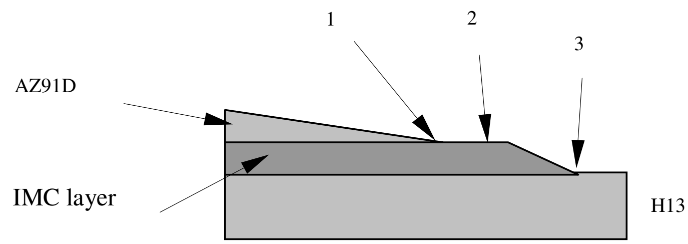


Figure 5 - Schematic of polishing preparation

The diffraction patterns at points 2 and 3 are simple. At point 2, only orthorhombic Fe_2Al_5 was detected. The high content of manganese in this phase, could be (Fe, Mn)$_2$Al$_5$ where Mn acts as substitution of some Fe atoms in the structure. At point 3, both (Fe,Mn)$_2$Al$_5$ and iron were detected. This is similar to Winkelman [8] summarised that in all cases of iron reaction with aluminium alloy melt, η-Fe_2Al_5 forms preferentially, due to the strong affinity of iron with aluminium.

For phases 1 and 2, though their compositions are different, they were identified as having the same structure, η-Fe_2Al_5. The one with higher Mn contents shows a lighter appearance and the other with higher Fe content, shows a darker appearance. Phase 3 looks like a crust on top of the inner (Fe, Mn)$_2$Al$_5$ with a much higher Mn content.

At point 1, the interface of the IMC layer and the AZ91D alloy, η-Fe_2Al_5, hexagonal Mg and F-phase $Mn_{23}Al_{77}$ as well as the β-$Mg_{17}Al_{12}$ were detected. So the Mn and Al rich crust is likely to be the F--phase $Mn_{23}Al_{77}$. The formation of this layer, though is very important in the growth of the IMC layer and the start of soldering, is still unclear. Knapp and Follstaedt[22] first found this phase produced by ion beam mixing of predeposited Al-Mn alloy. This phase forms when Mn content is higher than 21at. %. J. M. G. J. de Bakker and E. H. du Marchie van Voorthuysen[23] produced this phase by means of electron bombardment. Under all circumstances, this phase forms with quench effect. In this experiment, the F-phase forms from the liquid during cooling and formation of this phase indicate that there is rich Al and Mn at this area. From Figure6 the β-$Mg_{17}Al_{12}$ formed in contact with the top crust of the soldering layer which also indicate Al segregation in this area.

	Al	Fe	Mn	Others (Mg, Cr, Si, etc)
Phase 1	66.9	13.8	17.09	Balance
Phase 2	71.42	15.88	11.55	Balance
Phase 3	63.08	13.08	21.76	Balance

Table 3. Averaged composition (atm.%) of the IMC layer

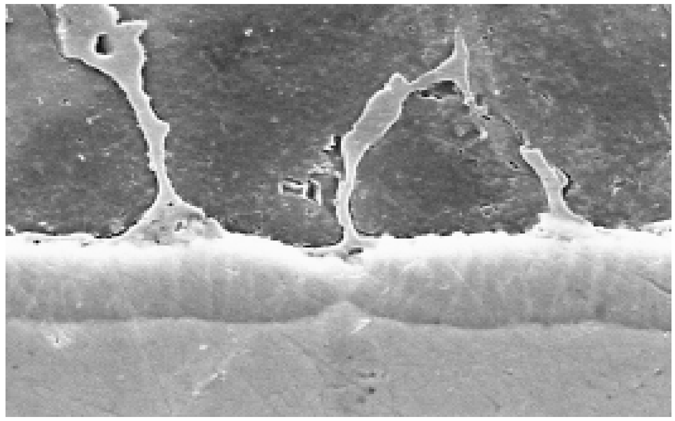


Figure 6 - Formation of β-$Mg_{17}Al_{12}$ at the IMC-cast alloy interface

(ii) Growth of the IMC layer

The thickness of this layer was expected to vary with dipping time, as in the case of aluminium alloys [6,8,19,24]. Figure 7 shows the averaged thickness of the soldered layer after dipping for up to three hours. It is clear that the relationship between the layer thickness and immersion time is linear. This is different from the relationship in the case of aluminium immersion [8] which is parabolic. It is believed [25 26]that the amount of Si in aluminium alloys may reduce the alloyed layer's growth rate with the increase of its thickness by either reducing the iron dissolution or increasing the diffusion of iron in the IMC to the melt leading to the dissolving of this layer. As the immersion time increases, the Si accumulates along the layer interface which impedes the chemical reaction and the growth of the intermetallic layer. In Mg-alloy immersion tests, for all time periods, the Si content in the intermetallic layer is very low and doesn't change much (at the level of 0.05%). No Si-contain binary or ternary Al-Si-third part was detected so its effect can be neglected. The linear growth rate of the IMC layer shows that the growth follows the equation $Y=Kt^n$, n=1. Such reactions, according to Guttmann, [27]are surface reaction controlled.

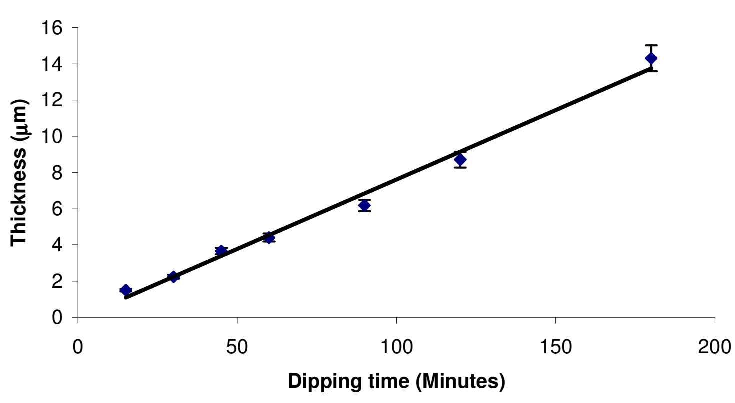


Figure 7 - Thickness of the IMC Layer

The growth and dissolution of the Fe_xAl_y intermetallic at the interface is described by Gopal [28]. The linear growth mode in this study is caused by the outer layer, the Mn rich layer. Because of the Mn-rich layer, the diffusion of iron atoms to the alloy melt is suppressed. The effect is similar to the suppressing of iron in the magnesium alloy by the addition of manganese. According to Lashko [16] when Mn content is over 0.1% in the Mg-Al-Mn alloy, the iron does not form an independent compound but is combined in the existing phases of Mn-Al system, replacing Mn atoms. Fe atoms diffusing to the Al-Mn layer then will be consumed in this layer preventing further diffusion. On the other hand, Al atoms diffusing to the substrate will firstly meet the Mn-rich melt and form a supersaturated layer in that area.

The formation of the IMC layers therefore consists the following steps:

- Nucleation of the Fe_2Al_5 compound due to the high affinity of Fe to Al

- Diffusion of Al atoms to the substrate surface causing Al supersaturation at the interface of Mg-alloy and the substrate.

- The formation of the high Mn phase which impedes the Fe diffusion to the alloy melt. The IMC growth is then based on the substitution of Fe atoms with Mn atoms.

- The supersaturating of aluminium at the interface of IMC layer and the melt causes the formation of β-$Mg_{17}Al_{12}$ and precipitation of the metastable F-phase.

3.2 Soldering formation in HPDC of AZ91D

3.2.1 Eject pin surface morphology

During HPDC of AZ91D experiment, the pins were coated with a grey thin film which is believed to be α-Mg. After about 12 shots, slight build up can be seen at the side of the pin. The build up materials then was cleared away by the next ejection before it appears again after 25-30 shots. Each time the build up forms, part of the build-up layer will be cleared away in the next few shots. Figure 8 shows the appearance of the die and pin as well as the build-up layer morphology on the pin surface. Soldering on the pin can be seen clearly. All the particles shown in Figure 6 are Al-Mn compounds.

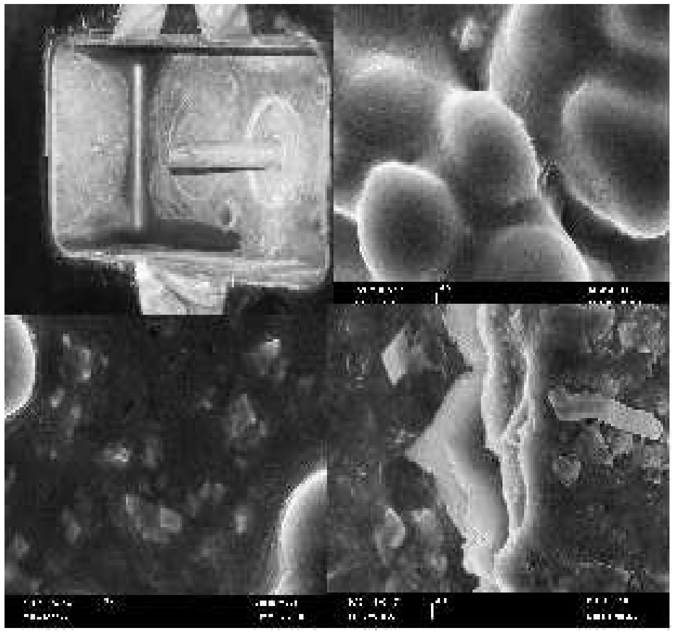


Figure 8 - Die cast pin surface morphology
Top-left: Pin & Die after 300 shots   Top-right: build-up dendritic α-Mg
Bottom left: Precipitated Al-Mn particles   Bottom right: Broken build-up layers

3.2.2 IMC layer composition

The die cast pins were cut and analysed with SEM and Edax. Fig 9 is an image of the sectioned pin. The composition of the IMC layer and the crust is listed in Table 4.

	Mg	Al	Mn	Fe	Others
IMC	2.79	74.91	12.17	9.54	Balance
Crust	3.27	63.06	32.28	1.30	balance

Table 4. Compositions of IMC layer and crust layer (at.%)

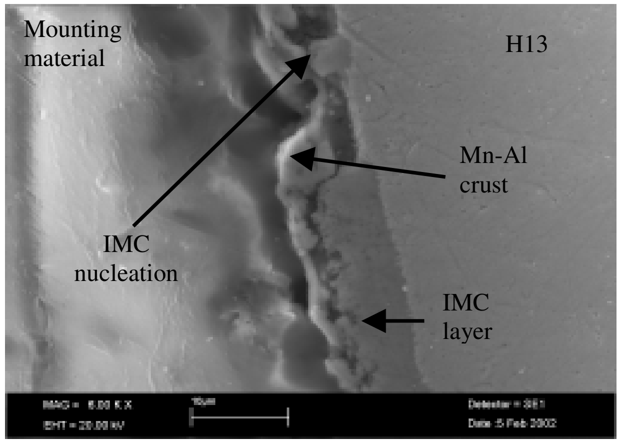


Figure 9 - IMC layer and the crust layer
(after 300 shots, etched in 10% Nital)

Comparing the composition of the IMC layer of the pin with that of the dipping sample, it can be concluded that this IMC layer is also $(Fe, Mn)_2Al_5$. The difference between the composition of the crust of the cast pin and the phase 3 of the dipping sample is that Mn content is higher and Fe content is lower in the crust than those in phase 3. A line scan shows that with increasing distance to the substrate surface, both Al and Fe contents decreased while Mn and Mg contents increased. This is attributed to the appearance of Mg in this layer. Each shot brings certain amount of Mg on the surface. Mg impedes the diffusion of iron into this layer, leading to a less substitution of Fe by Mn atoms. Then the phase should still be the same as in immersion test, the F-phase, $Mn_{23}Al_{77}$.

It is noted that after each casting cycle, the next injection of Mg alloy liquid will impinge the die surface. The temperature in the shot sleeve is not high enough to melt the solidified layer on the pin surface. This is the same as is happened in the aluminium die casting[3]. In this case, the growth of the soldering layer is also occurring in the solid state.

3.2.3 Summary of the solder formation

From the above analysis, it is clear that the formation of the soldering happens in the following order:

- Nucleation of the Fe_2Al_5 compound. During solidification of each casting, any Mg left as coating on the die surface will be broken by the next shot because of the impingement of solid Al-Mn particles in the liquid melt.

- Al and Mn diffusion to Fe_2Al_5 compound and casting alloy liquid interface causing growth of Fe_2Al_5 and segregation of Mn-Al compound

- Diffusion of Fe to the solid-liquid interface and substitute some of the Mn atoms.

4. Conclusion

A series of experiments was performed to investigate soldering in HPDC of Mg alloys. The results shows:

- Soldering in magnesium alloy die casting is a series reactions between Al, Mn and Fe. Mn has a positive effect in this reaction.
- Mg impedes the reaction by preventing the diffusion of Fe to the casting alloy.
- The soldering layer is separated into two phases: the orthorhombic η-$(Fe, Mn)_2Al_5$ and the F-phase, $Mn_{23}Al_{77}$, which is formed during cooling of the system.
- The growth rate of the IMC layer in the immersion test is linear.

5. Acknowledgment

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