Corrosion and Stress Corrosion Cracking of New Wrought Magnesium Alloys

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New magnesium alloys (Die-Cast and wrought) have increasingly been developed in recent years for the automotive industry due to their high potential as structural materials for low density and high strength/weight ratio demands. However, their poor mechanical properties and low corrosion resistance have led to a search for new kinds of magnesium alloys with better strength, ductility, high temperature behaviour and high corrosion resistance. The main objective of this research is to investigate the corrosion behaviour of new magnesium alloys: Mg-Al-Ca, Mg-Al-Sr, Mg-Zn-Mn-Si (ZSM) and Mg-Zn-Mn-Si-Ca (ZSMX). These ZSM6X1 and ZSM651+YCa alloys were prepared using hot extrusion. These Mg-Al-Ca and Mg-Al-Sr were prepared using high pressure die cast. AC and DC polarization tests were carried out on the new alloys. Microstructure was examined using optical and electron microscopy (SEM) and EDS. The addition of Si increased the corrosion resistance. The additions of Sr and Ca also affected the corrosion behaviour. These results can be explained by the effects of alloying elements on the microstructure of Mg alloys such as grain size and precipitates caused by the change in precipitation and recrystallisation behaviour.

Keywords: Magnesium Alloy, Die Cast, Hot Extrusion, Alloying Element, Electrochemical Techniques.

Introduction

In the manufacture of transport, weight reduction through the use of lightweight materials remains a very successful and simple means of improving fuel economy and reducing harmful emissions. High-purity magnesium alloys are now sophisticated materials that provide significant opportunities for weight reduction and therefore real scope to achieve these environmental goals. Increases in magnesium alloys for automotive applications have driven the substantial increase in magnesium world demand; in particular, magnesium alloys for making die-cast components. According to Australian Magnesium Corp Ltd (AMC), die-cast magnesium automotive components account for ~150,000 t/y of magnesium alloys and dominate the application of magnesium die-castings. This substantial and sustained increase in magnesium consumption has led to significant changes in the magnesium manufacturing industry and has encouraged suppliers to develop their processes and alloys and identify potential future applications of magnesium for both cast and wrought products. Casting of magnesium is a very economic process, particularly die-casting, and suitable for mass-volume component production, but even at low volumes it also provides substantial opportunity to integrate one or more parts together and produce with complex geometries.

Mg-Al alloys such as AM50, AM60 and AZ91 have been used extensively as these alloys exhibit superior die castability and have a good balance of strength and ductility. However, the high temperature mechanical properties of commercial magnesium alloys are poor due to the presence of the Mg17Al12 phase that shows poor thermal stability. So the application temperature of these alloys is generally limited to around 100°C [1, 2]. Therefore, the demand for new magnesium alloys to solve these problems is increasing [3]. In this study, Ca and Sr, which are known to produce thermally stable precipitates such as Al4Ca, Al2Mg13Sr and Al4Mg13Sr, were chosen as alloying elements. Calcium is an element which is more economical and lighter than the rare-earth (RE) elements. The Mg-Al-Sr alloys were also developed to replace the expensive RE elements which are added to improve high temperature resistance. The Sr content was also raised to avoid any Al supersaturation [4, 5].
However, there is a growing need for high strength wrought Mg alloys in the automotive and aerospace industries. Four different alloy systems have been mainly utilized for the development of the wrought Mg alloys, i.e., Mg-Zn, Mg-Al, Mg-Th, and Mg-Mn alloys [6]. Among these, Mg-Zn alloys were found to have a large age hardening response stemming from the precipitation of a transition phase ($\beta'$), and consequently offered a combination of good strength and ductility [7, 8]. It has been reported, however, that grain refinement is difficult to achieve in Mg-Zn alloys [6]. Several alloying elements, including Zr, rare-earth (RE), and Cu, have been added to Mg-Zn alloys to improve the mechanical properties; Zr for grain refining and strengthening [9], RE for improved high temperature properties [10], and Cu for ductility improvement [11].

Mg-Zn-Si series is a new promising alloy system developed to meet the above requirements. The silicon addition to magnesium alloys causes an increased fluidity of the molten metal. The Mg$_2$Si formed by the addition of Si exhibits high melting point (1085°C), high hardness (460 HV), low density (1.9 g cm$^{-3}$), high elastic modulus (120 GPa), and low thermal expansion coefficient (7.5 x 10$^{-6}$ K$^{-1}$) [12]. This intermetallic phase is very stable and can impede grain boundary sliding at elevated temperatures. Guangyin et al [13]. Investigated the microstructural features, tensile properties at both ambient and elevated temperature of 150°C, impact strength, and creep resistance to get a better overall understanding of alloys in this system. They identified the most promising compositions as those of Mg–Zn–Si alloyed with Ca. But up to now, limited research has been carried out on the electrochemical behaviour of this system.

The main objective of this research is to investigate the corrosion behavior of new magnesium alloys due to different processing for the transportation industry (i.e., Die cast and wrought). And the relation between processing, microstructure and corrosion behavior of the new alloys.

**Experimental Procedures**

In this study, all test specimens of the Mg-Al-Ca and Mg-Al-Sr alloys were die-cast on a 320 ton high pressure die-casting machine. The alloy designations and chemical analysis results of these specimens as examined by spectrometer are summarized in Table 1.

Mg-Zn alloys were melted in a low carbon steel crucible and melt surface was protected with a gas mixture of CO$_2$+0.5% SF$_6$. The alloying elements Zn, Ca and Mn with 99.99% purity were added to the melt. Silicon was added to the melt in the form of Mg-10 wt% Si mother alloy. The alloy designations used in the present study are listed in Table 2. The ingots were homogenized at 400°C, water-cooled, and subsequently scalped to give 80 mm diameter billets. After preheating, the billets were extruded at 300°C for ZSM and ZSMX, with an extrusion ratio of 25:1 to give 16 mm diameter cylindrical rods.

The microstructure was examined by optical microscopy and scanning electron microscopy (SEM) with EDS. The existence and distribution of the second phases were examined by X-ray and EPMA. Specimens for optical microscopy were mechanically polished followed by chemical etching with a 1% HNO$_3$ + 24% distilled water + 75% diethylene glycol solution.

The electrochemical behaviour of die cast and extruded magnesium alloys was investigated using linear polarization (LP), Potentiodynamic polarization (PD) measurements (DC polarization) and Electrochemical Impedance Spectroscopy (EIS). All the electrochemical measurements performed in 3.5% NaCl saturated with Mg(OH)$_2$, with a pH = 10.5 at which Mg can cover itself with more or less protective oxide or hydroxide which checks the dissolution reaction [14]. The electrochemical testing was employed to study the main features of the processes taking place at the alloy/solution interface. The effect of alloying elements on the corrosion resistance was studied. The corrosion resistance of Mg alloys was pointed out by EIS measurements performed during the free immersion time and the effect of the different alloying elements was studied. The behaviour of the electrode/electrolyte interface at different immersion times was also studied. Corrosion rates were derived from polarization data by the common method [15]. For all measurements a three-electrode electrochemical cell was used, with an SCE as reference electrode and a platinum counter electrode. The working electrode...
was prepared from the Mg-alloy samples embedded in an acrylic resin to provide electrical isolation of the sample surface. The samples were air dried at room temperature. The linear curves were obtained using a 273A EG&G Potentiostat/Galvanostat, with a voltage scan rate of 0.5 mV/s during 4 hr of immersion. The impedance measurements were carried out using a PARSTAT 2263 frequency response analyser coupled with the potentiostat. All the experiments were controlled by a PC, which was also used for the collection, storage, and plotting of data. The scanned frequency ranged from 6 mHz to 100 kHz and the perturbation amplitude was 5 mV (it was observed that a variation of the amplitude did not change the frequency response of the electrode/electrolyte interface). The impedance measurements were performed at open circuit potential ($E_{oc}$). A partial data fitting made with the Boukamp circuit equivalent software [16] for the charge transfer process produced the $R_p$ (polarization resistance) and $C_{dl}$ (double-layer capacitance) values.

Results and Discussion

New Die Cast Alloys based on Mg-5%Al

Microstructure Analyses

The microstructures of the Mg-5wt.% Al-xwt.% Ca (Mg-5Al-xCa) alloys are shown in Fig. 1. The comparisons of Figs. 1(a)–(d) reveal that the major changes caused by the addition of Ca is the formation of precipitates and a reduction in grain size. As shown in Fig.1, the average grain size decreased with increasing Ca content. Most of precipitates were observed at grain boundaries. Figures 2(a)–(c) show a difference in the microstructure according to the different amounts of Sr in the Mg-5Al alloys. As in the addition of Ca, the addition of Sr reduced the grain size and formed precipitates at grain boundaries. The comparison of the results in Fig. 1 and Fig. 2 indicates that the Ca addition produced more second precipitates along the grain boundary than the Sr addition. It could also be seen that adding Ca had a greater effect in grain refinement than adding Sr. These results are expected to affect the corrosion behavior of the Mg-Al alloys.

Figure 3 shows the X-ray diffraction patterns for the Mg-5Al-2.0Ca and Mg-5Al-1.5Sr alloys. By analyzing these results, it was confirmed that the second phases formed by adding Ca were Al2Ca and Mg2Ca compounds and those formed by adding Sr were AlSr and Al3Mg13Sr compounds [5]. Since these precipitates are more stable at elevated temperatures than the Mg17Al12 phase, they are expected to improve the high temperature mechanical properties of the Mg-Al alloys.

Figures 4 and 5 show the scanning electron micrographs of the as-cast Mg-5Al alloys with different amounts of Ca and Sr. From these results and the XRD patterns in Fig. 3, it was confirmed that the second phases formed by adding Ca and Sr were Al2Ca, Mg2Ca, Al4Sr and Al3Mg13Sr compounds, which are more stable at elevated temperatures than the Mg17Al12 phase. As shown in Fig. 5, the second phases formed by adding Sr

![Fig. 1. Microstructures of the die-cast Mg-5Al-xCa alloys: (a) Mg-5Al, (b) Mg-5Al-1.0Ca, (c) Mg-5Al-1.5Ca and (d) Mg-5Al-2.0Ca.](image-url)
were precipitated along the grain boundary, and the Mg$_{17}$Al$_{12}$ phase was also observed. However, the precipitates formed by adding Sr appeared to be less continuous at the grain boundary than those formed by adding Ca. In order to make a close investigation into the distribution of precipitates, EPMA analyses of the Mg-5Al-1.5Ca and Mg-5Al-1.5Sr alloys were carried out. These results showed that most of the Al, Ca and Sr were evenly distributed at grain boundaries. But the Mg-5Al-1.5Sr alloy showed less uniform distribution than the Mg-5Al-1.5Ca alloy. The precipitates in the Mg-5Al-1.5Sr alloy tended to concentrate at the node of grain boundaries. It is postulated that these results might affect the corrosion behavior of the Mg-Al alloys.

**Corrosion Behavior**

The potentiodynamic curves obtained for Mg-5Al containing different quantities of Ca or Sr are shown in Fig. 6. The effect of the alloying element (Ca or Sr) on the corrosion behaviour can be seen. The corrosion parameters estimate the effect of the alloying element, which means increasing the anodic current densities and the ennobling of the potential values.
The effect of Ca or Sr on the corrosion rate of the Mg-5%Al alloy is shown in Fig. 7. As shown in this figure, the addition of Ca or Sr increases the corrosion rates of the Mg-5%Al alloys. This behaviour of the alloys containing different amount of Ca or Sr is due to the different microstructure and distribution of the second phases. As the alloying elements additions increased the grain size decreased and more precipitate were distribute in the grain boundaries (in case of Ca) or in the grain (in case of Sr). A high quantity of second phases at the surface creates more microgalvanic sites. Therefore, high Ca or Sr content in Mg–5%Sr alloy decreases the corrosion resistance. However in case of 1.8 wt.% of Ca the distribution of the second phases rich with Al close to continuously. Due to high content of Al in the grain boundaries this area acts as a corrosion barrier [17].
It was found that the high temperature mechanical properties of the Mg-5%Al alloys were significantly improved by addition of Ca or Sr [18]. From our corrosion study we found that the corrosion behaviour of the Mg-5%Al alloys were decreased. However, the behaviour of the alloy containing 2% Ca (Mg-5%Al-2%Ca) was similar to the alloys without Ca (Mg-5%Al). For industrial application the Mg-5%Al-2%Ca alloy exhibit combination of high thermal stability and high corrosion resistance. In comparison between the behaviour of the alloys containing Ca or Sr, the alloys containing Ca exhibit higher corrosion resistance due to the Al supersaturation in the Mg matrix and increased the matrix potential. However addition of Sr avoids any Al supersaturation [19]. Addition of Sr decreased the contents of $\beta$ phase. The distribution of $\beta$ phase was none contentiously due to this $\beta$ phase act as a galvanic site. Furthermore, when the content of Sr was 1.5% the second phases rich with Al and Sr were observed in the grain boundaries and less $\beta$ phase was observed in comparison to the other alloys containing Sr. More contentiously phases rich with Al in the grain boundaries and less non contentiously $\beta$ phase increased the corrosion resistance of the Mg-Al-Sr.

![Fig. 7. Corrosion rate from potentiodynamic polarization as function of (a) Ca contents for Mg-5Al-xCa and (b) Sr contents for Mg-5Al-xSr alloys.](image)

![Fig. 8. Typical microstructure of extruded Mg alloys; (a) ZM60, (b) ZSM600, (c) ZSM610 and (d) ZSM620.](image)
New Extruded Alloys based on Mg-6%Zn

Microstructure Analyses

The microstructure of the as-extruded ZM60, ZSM600, ZSM610, and ZSM620 alloys is shown in Fig. 8. The average grain sizes of the extruded ZSM alloys were 23 μm, 12.1 μm, 11.3 μm, and 10.3 μm, respectively. As shown in the SEM analysis in Fig. 9, fine Mg$_2$Si phases are distributed parallel to the extrusion direction in the ZSM610 alloy. Also, the type of the Mg$_2$Si particles was polygonal script. Therefore, the grain refinement of the Mg-Zn-Mn-Si alloy can be explained as grain growth which is suppressed by the formation of precipitates containing Mg and Si during recrystallization. The Mg$_2$Si polygon was created by breakage of the Chinese type M$_g$Si during the extrusion process. The polygonal type Mg$_2$Si phases are dispersed parallel to the extrusion direction in the as-extruded ZSM alloys.

Corrosion behaviour

The Nyquist plots of Mg-Zn-Mn alloys containing different quantities of Si at open circuit exhibit one capacitive loop (Fig. 11).

The Nyquist diagrams obtained at the potential of open circuit present a capacitive loop at high and
intermediate frequencies. In addition, at low frequencies a small capacitive loop was always observed for two of the samples (ZM60 and ZSM610), this loop being more or less reproducible. The EIS data for the first capacitive loop associated at the transfer charge process can be fitted with the Boukamp circuit equivalent [15], the equivalent circuit consisting of a $R_p$ and a $C_{ld}$ in parallel.

The obtained $I/R_p$ (which is proportional to the corrosion rate) is plotted as a function of Si contents (Fig. 12), for ZSM6X0 alloys. Moreover, the corrosion rate values determined on the linear polarization curves (DC measurements) are regrouped in Fig. 12. It can be seen that the maximal $I/R_p$ value is obtained for the alloys containing 0.5 wt% of Si (ZSM600). Thus, the $I/R_p$ values obtained on the EIS measurements pass over the maximum increase in Si contents, in the same way as the corrosion current determined on the DC polarization.

It is known that silicon has little deleterious effect on the basic salt-water corrosion performance of pure magnesium because the electrochemical potential of the Mg$_2$Si precipitate (-1.65 V SCE) is similar to that of magnesium (-1.66 V SCE). However, the corrosion behaviour of ZSM6X0-extruded magnesium alloys is influenced by the size and the quantity of Mg$_2$Si particles. The Mg$_2$Si phase plays a dual role, depending on its volume fraction ($f = V_{Mg2Si}/V_{al}$) in the microstructure. As $f$ increased (from Chinese Script Type in ZSM600 to Polygonal type in ZSM620 — Fig. 8) the corrosion resistance increased also. Moreover, Si additions may affect the corrosion behaviour by surface oxidation [20].

The potentiodynamic curves obtained for Mg-Zn-Mn-Si containing different quantities of Ca alloys as a function of Ca contents are shown in Fig. 13. The effect of the alloying element (Ca) on the corrosion behaviour can be seen. The corrosion parameters estimate the effect of the alloying element, which means increasing the anodic current densities and the desensitizing of the potential values. The effect of calcium on the corrosion rate of the ZSM651 alloy is shown in Fig. 14. As shown in this figure, the addition of calcium increases the corrosion rates of the ZSM651 + YCa alloys.

High Ca content (Si content is constant) increases the quantity and size of the CaMgSi phase. This phase has a potential difference higher than the magnesium matrix. A high quantity of CaMgSi at the surface creates more microgalvanic sites. Therefore, high Ca content in Mg–Zn–Mn–Si alloy decreases the corrosion resistance. We
proven this phenomenon by EIS and Scanning Kelvin Probe Force Microscopy [20].

Conclusions

New Die cast alloys

The effects of the Ca and Sr addition on the corrosion properties of the Mg-5wt.% Al alloys were investigated. The following conclusions can be made from the present study:

- The major changes in the microstructure of the Mg-5Al alloy by the addition of Ca and Sr were the formation of Al2Ca, Mg2Ca, Al2Sr and Al3Mg13Sr precipitates and a reduction in grain size. It was found that adding Ca had a greater effect in grain refinement than adding Sr.
- It was found that the corrosion behavior of the Mg-5Al alloys decreased by the addition of Ca or Sr.

New Extruded alloys

The effects of the Si and Ca addition on the corrosion properties of the Mg-Zn-Mn-Si-Ca alloys were investigated. The following conclusions can be made from the present study:

- The grain size of the Mg–6%Zn alloy was significantly refined with the addition of silicon and calcium in the as-extruded condition.
- The addition of silicon decreased the corrosion rates of the ZSM6X0 alloys. It is known that silicon has little deleterious effect on the basic salt-water corrosion performance of pure magnesium because the electrochemical potential of the Mg2Si precipitate (-1.65V .SCE) is similar to that of magnesium (-1.66V .SCE).
- The addition of calcium to the Mg–6% Zn–1% Mn–5% Si alloy decreased the corrosion resistance. Due to the formation of cathodic sites between the magnesium matrix and the CaMgSi intermetallics.

References