THE ROLE OF ALLOYING ELEMENTS ON THE CORROSION BEHAVIOR OF NEW WROUGHT Mg-Zn BASED ALLOYS

G. Ben-Hamu¹, D. Eliezer¹ and K. S. Shin²

¹Department of Materials Engineering, Ben-Gurion University of the Negev Beer-Sheva, Israel
²School of Materials Science and Engineering, Research Institute of Advanced Materials Seoul National University, Seoul, Korea

ABSTRACT. The development of new wrought magnesium alloys for automotive industry has increased in recent years due to their high potential as structural materials for low density and high strength/weight ratio demands. However, the poor mechanical properties and low corrosion resistance of the magnesium alloys have led to search a new kind of magnesium alloys for better strength, ductility and high corrosion resistance. The main objective of this research is to investigate the mechanical properties and the corrosion behavior of new magnesium alloys; Mg-Zn-Ag (ZQ) and Mg-Zn-Si-Ca (ZS) alloys. The ZQ6X and ZS6X-YCa alloys were prepared by using hot extrusion method. Hardness AC and DC polarization tests were carried out on the extruded rods, which contain different amounts of silver or silicon and calcium. The potential difference in air between different phases and the matrix was examined using scanning Kelvin probe force microscopy.

The microstructure was examined using optical and electron microscopy (TEM and SEM), x-ray analysis and EDS. The results showed that the silver addition improved the mechanical properties but decreased the corrosion resistance. The addition of silicon and calcium also affected both mechanical properties and corrosion behavior. These results can be explained by the effects of alloying elements on microstructure of Mg-Zn alloys such as grain size and precipitates caused by the change in precipitation and recrystallization behavior.

Keywords: Mg-Zn alloys; Corrosion behavior; hot extrusion method; Micro-Hardness; TEM; Electrochemical techniques.

Introduction

The interest in lightweight materials in the structural applications has increased significantly due to their importance in the environmental and energy saving problems. Especially in the automotive industry, magnesium alloys, due to their low density and high specific strength, have become the key materials for enhancing the fuel efficiency. In fact, there has been a rapid growth in the structural applications of magnesium alloys during the past decade. However, the majority of this growth has been in the area of die-cast components and some semi-solid formed components [1]. In contrast, wrought magnesium alloys are used to approximately only 1% of total magnesium consumption. There are two major technical issues in order to expand the wrought magnesium market. First is a low production rate. A typical magnesium alloy must be extruded 5-10 times slower than a typical aluminum alloy. Second is a development of new wrought magnesium alloys with a combination of high strength, high ductility and high corrosion resistance.

In recent years, the modification of alloy composition and/or heat treatment has been attempted for improved mechanical properties [2-4] and corrosion resistance [5-8] in the casting alloys. However, there is a growing need for high strength wrought Mg alloys in the automotive and aerospace industries. Four different alloy
systems have mainly been utilized for the development of the wrought Mg alloys, i.e., Mg-Zn, Mg-Al, Mg-Th, and Mg-Mn alloys [9]. Among these, Mg-Zn alloys were found to have a large age hardening response, stemming from the precipitation of a transition phase (β'), and consequently offered a combination of good strength and ductility [10-15]. It has been reported, however, that grain refinement is difficult to achieve in Mg-Zn alloys [9]. Several alloying elements, including Zr, RE and Cu, have been added to Mg-Zn alloys to improve the mechanical properties; Zr for grain refining and strengthening [16,17], rare-earth (RE) for improved high temperature properties [17-19] and Cu for ductility improvement [20,21].

Mg-Zn-Si series is a new promising alloy system which is developed to meet the above requirements. The silicon addition to magnesium alloys causes an increased fluidity of the molten metal. The Mg2Si formed by the addition of Si exhibits high melting point (1085 °C), high hardness (460 HV0.3), high elastic modulus (120 GPa) and low thermal expansion coefficient (7.5 x 10^-6 K^-1) [22]. This intermetallic phase is very stable and can impede grain boundary sliding at elevated temperatures. Yuan Guangyin et al [23] investigate the micro structural features, tensile properties at both ambient and elevated temperature of 150 °C, impact toughness and creep resistance in order to get a better overall understanding of alloys in this system. They identify the most promising compositions Mg-Zn-Si alloyed with Ca. But up to now, limited research has been carried out on the corrosion behavior of this system.

The objective of the present study is to develop new wrought Mg alloys with improved strength and ductility and investigate the corrosion resistance of the new alloys. The effects of Ag or Si and Ca addition of the new Mg-Zn-Ag and Mg-Zn-Si-Ca alloys were examined.

**Experimental Procedures**

Mg-Zn alloys were melted in a low carbon steel crucible and melt surface was protected with a gas mixture of CO2+0.5% SF6. The elemental Zn, Ag and Ca 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 as follows; Mg-6%Zn for Mg-6 wt.% Zn, ZQ6x for Mg-6 wt.% Zn-x wt.% Ag and ZSM6x1-yCa (ZSMX) for Mg-6 wt.% Zn-1 wt.% Mn-x wt.% Si-y wt.% Ca. Maximum impurity levels: 0.004 wt% Fe, 0.005 wt% Ni, 0.05 wt% Cu. The ingots were homogenized at 400°C, water-cooled, and subsequently scalped to give 80mm diameter billets. After preheating, the billets were extruded with an extrusion ratio of 25:1 to give 16mm diameter cylindrical rods.

Hardness tests were carried out in order to evaluate the micro-hardness characteristics with a Vickers hardness tester under an applied load of 200 grf and holding time of 15 sec.

Specimens for optical microscopy were mechanically polished followed by chemical etching with a 1% HNO3 + 24% distilled water + 75% diethylene glycol solution. Thin foils for transmission electron microscopy (TEM) were prepared by chemical etching in a 5% HNO3 + ethanol solution below 0°C.

The behavior of both Mg-Zn-Ag and Mg-Zn-Mn-Si-Ca magnesium alloys was investigated by using potentiodynamic polarization (PD) measurements, linear polarization (LP) measurements (DC polarization) and electrochemical impedance spectroscopy (EIS).

All the electrochemical measurements were 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 [24].
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 Mg-Zn alloys corrosion resistance was studied. The corrosion resistance of Mg alloys was pointed out by EIS measurements performed during the free immersion time and under polarization and the effect of the different alloying elements was studied. The evolution of the electrode/electrolyte interface at different immersion times was also studied. Corrosion rates were derived from polarization data by the common method [25].

The electrochemical tests using both DC (potentiodynamic and linear polarization) and AC techniques (EIS) were carried out in 3.5% NaCl saturated with Mg(OH)₂. 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. Mg-alloy samples were embedded in an acrylic resin to provide electrical isolation of the sample surface. The samples were air dried at room temperature.

The potentiodynamic and linear curves were obtained using a 273A EG&G Potentiostat/Galvanostat, with a voltage scan rate of 0.5 mV/s. 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 acquisition, storage and plotting of data. The scanned frequency ranged from 6 mHz to 100 kHz and the perturbation amplitude was of 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 [26] for the charge transfer process produced the R_p (polarization resistance) and C_{dl} (double-layer capacitance) values.

Results and Discussion

Microstructure and mechanical properties of the extrusions alloys:
Figure 1 shows the microstructures of the Mg-6%Zn and ZQ63 alloys in the as-extruded condition. The recrystallized grain structures were observed, particularly in the Mg-6%Zn alloy, where the growth of recrystallized grains was evidenced. It was also shown that, the grain size of the extruded alloy was markedly reduced with the addition of Ag to the Mg-6%Zn alloy. The average grain sizes of the Mg-6%Zn and ZQ63 alloys were found to be 7μm and 2μm, respectively. The grain refinement found in the Ag containing alloys appeared to be caused by the suppression of dynamic recrystallization and grain growth, during the extrusion caused by the formation of precipitates at grain boundaries.

![Fig. 1. Microstructures of the as-extruded alloys: (a) Mg-6%Zn (b) ZQ63](image)
Fig. 2. Effect of Ag addition on the micro-hardness of Mg-Zn extruded alloys.

The micro-hardness behavior of the Mg-Zn alloy is known to be caused by the precipitation of (B') phase [8-13]. Figure 2 shows the effect of Ag addition on the micro-hardness of Mg-Zn extruded alloys. High content in Ag addition increases the micro-hardness of the ZQ6X alloys. Figure 3 shows the microstructures of the ZSM631+0.4Ca (3 wt.% Si and 0.4 wt.% Ca), ZSM651+0.8Ca and ZSM6101+0.4Ca alloys in the as-extruded condition. From these microstructures, it can be seen that the addition of Si suppressed the grain growth during the extrusion process. However, the suppressed of the grain growth influences by the addition of Ca more than the addition of Si to Mg-Zn-Mn alloy (Fig. 4)

Fig. 3. Microstructures of the as-extruded alloys: (a) ZSM631+0.4Ca (b) ZSM651+0.8Ca (c) ZSM6101+0.4Ca
Figures 5 show the TEM micrographs obtained from the ZSM651+0.4Ca alloy. It can be seen from the figure the precipitate of CaMgSi.

**Corrosion behavior of the extrusions alloys:** Potentiodynamic polarization (PD) measurements, linear polarization (LP) (DC polarization) and electrochemical impedance spectroscopy (EIS) tests were used in this work in order to understand the effects of the Ag or Si and Ca addition on the corrosion resistance of the Mg-Zn alloys. Figure 6 shows the effect of Ag addition on the corrosion resistance of the Mg-6%Zn alloy. The addition of silver to the Mg-Zn alloys increased the corrosion rates of the extrusions. This increase in corrosion rate by Ag addition to the Mg-Zn alloy is considered to be caused by the formation of micro-galvanic cell between the $\alpha$-Mg (solid solution) and the precipitates of Mg-Ag ($\text{Mg}_{54}\text{Ag}_{17}$) due to their different electrochemical potentials [27].
Fig. 6. Effect of Ag addition on the corrosion rates (linear polarization methods) of Mg-Zn extrusions after immersion test at different time.

Figure 7 shows the effect of silicon on the corrosion rate of the Mg-6%Zn-1%Mn alloy. As shown in the figure, the addition of silicon decreased the corrosion rates of the ZSM6x1+0.4Ca alloys. It is known that silicon has little deleterious effect on the basic saltwater corrosion performance of pure magnesium because the electrochemical potential of the Mg$_2$Si precipitate (-1.65V$_{SCE}$) is similar to that of magnesium (-1.66V$_{SCE}$) [28]. Figure 8 shows the effect of calcium on the corrosion rate of the Mg-6%Zn-1%Mn-5%Si alloy. As shown in the figure, the addition of calcium increases the corrosion rates of the ZSM651+YCa alloys. High content of Ca and Si at Mg-Zn-Mn alloy create more sites of CaMgSi phase in the grain. This sites active cathodic to the Mg matrix [29].

Fig. 7. Corrosion rate (-l/Rp) from EIS measurements and Corrosion rate from linear polarization and potentiodynamic methods vs. Si contents of ZSM6XI+0.4Ca Mg alloys in 3.5% NaCl saturated with Mg(OH)$_2$. 
Fig. 8. Corrosion rate (\(\sim l/R_p\)) from EIS measurements and Corrosion rate from linear polarization and potentiodynamic methods vs. Ca contents of ZSM651+YCa Mg alloys in 3.5% NaCl saturated with Mg(OH)\(_2\).

Figure 9 shows the effect of extrusion process on the corrosion behavior of ZSMX alloys. The effect of Si and Ca was similar in the surface and the bulk of the extrusion pipe. Due to the different residual stress in the surface and the bulk of the extrusion pipe [30] the values of the corrosion rate not the same.

Fig. 9. The influence of the extrusion process on the corrosion behavior of ZSMX Mg alloy

Conclusions
1. The grain size of the Mg-6%Zn alloy was significantly refined with the addition of silver or silicon and calcium in the as-extruded condition.
2. The hardness of the Mg-6%Zn alloy increased with the addition of Ag. However, decrease the corrosion behavior.
3. The addition of silicon to the Mg-6%Zn alloy increased the corrosion resistance.
4. The addition of calcium to the Mg-6%Zn-5%Si alloy decreased the corrosion
resistance.
5. The extrusion process influences on the corrosion behavior of ZSMX alloy due to the residual stress on the surface of the extrusion pipe

REFERENCES