

# The Corrosion Behaviours of AZ61 Magnesium Alloy with the Ca Addition

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**Abstract**—the corrosion behaviors of AZ61 magnesium alloy with the Ca addition have been studied in this paper. These alloys were prepared in an induction melting furnace with an Al<sub>2</sub>O<sub>3</sub> crucible under a mixed atmosphere of CO<sub>2</sub> and SF<sub>6</sub>. The corrosion tests were completed using immersing in 0.5% and 3.5% NaCl solution for 4 hours at room temperature with no stirring. The phase analysis was performed by XRD. Olympus optical was used to characterize the microstructure and phases of magnesium alloys. Scanning electron microscopy was used to exhibits the morphologies of corroded surfaces of magnesium alloys after removal of the corrosion products. The results exhibited that with the addition of alloy element Ca, the microstructure of AZ61 magnesium alloy was remarkably refined, and the spotted, high-melting point phase Al-Ca intermetallic compounds can be found. With the addition of different content Ca, the corrosion behavior of AZ61 alloy decreases firstly and then increases sharply. When the content of Ca is 1%, AZ61 magnesium alloy shows the lowest corrosion rate. And the corrosion rate of AZ61-1% Ca alloy is 2.19 and 2.87 mm/a at 0.5% and 3.5% NaCl solution respectively.

**Keywords**—magnesium alloy; AZ61; corrosion behavior; alloy element Ca; microstructure (key words)

## I. INTRODUCTION

Magnesium alloys have been widely used in the fields of automobile manufacturing, aerospace industries and electronic industry, due to their advantages of low density, high specific strength and good recycling potential [1-5]. Among the Mg alloys, Mg-Al alloy is the commercially used magnesium alloy for automotive application. Corrosion is a based concern which prevents the wide spread applications of Mg alloys as a structural metallic materials. In all magnesium alloy, Mg-Al series alloy exhibits excellent corrosion resistance due to the high percentage of Al. In the as-cast Mg-Al series alloys, the addition of minor Ca is believed to be a beneficial method

to improve their corrosion resistance and mechanical properties [6-8]. When the alloy element Ca is used to modify the corrosion properties, microstructure changes are inevitable. Attempts have been made to change the microstructure of Mg-Al alloys by introducing thermally stable intermetallics through addition of special alloying elements and thereby improving its corrosion performance. These additions may introduce various thermally stable intermetallics in the microstructure [9-10]. Since the corrosion behaviors of AZ61 magnesium alloy is highly sensitive to microstructure, these intermetallics definitely play an important role in the properties [11]. In this work, the influence of minor Ca additions on the corrosion behaviors of AZ61 magnesium alloy was studied by immersion in 0.5 and 3.5% NaCl solutions.

## II. EXPERIMENTAL

### A. Materials preparation electing a Template

Commercial pure metallic Mg, Al, Zn and Mg-20 wt.% Ca master alloy were used as raw materials in this experiment. Five alloys of basic composition of Mg-6 wt.% Al-0.6wt. % Zn (AZ61 alloy) with the additions of 0, 0.5, 1, 1.5 and 2 wt. % Ca were prepared. All the raw materials should be dried at 200°C before smelting. These alloys were prepared in an induction melting furnace with an Al<sub>2</sub>O<sub>3</sub> crucible under a mixed atmosphere of CO<sub>2</sub> and SF<sub>6</sub> with the ratio of 100:1. The temperature was held at 710°C for 15 min to make completely dissolving of elemental Ca. Then the metallic liquid was poured into a metallic mold at 690–700°C. Experimental samples were machined from the casting samples. Then these samples were covered with MgO, heated at 420 °C about 20 h for solution treatment, and then quenched in water. Artificial aging treatments were completed at 200 °C for 10 h.

### B. Corrosion tests

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The metallic specimens for immersion corrosion tests were cut into coupons, 3-5 mm in thickness and 15-18 mm in diameter. Then these specimens were ground with 320grit  $\text{Al}_2\text{O}_3$  water proof abrasive paper, washed in distilled water, and degreased with alcohol. The specimens were immersed in 0.5% and 3.5% NaCl solution for 4 hours at  $25\pm 2^\circ\text{C}$  with no stirring. Corrosion products were removed by immersion in distilled water at room temperature for 10 min, and the materials loss was determined by electronic balance with a resolution of 0.1mg. The corrosion rate can be obtained through the following formula:

$$CR = 365 \times 24 \times 1000 (G_0 - G) / (\rho S t) \quad (1)$$

where  $CR$  is the corrosion rate (mm/a),  $G_0$  is the weight of metallic samples before corrosion immersion test (g),  $G$  is the weight of metallic samples after corrosion immersion test (g),  $\rho$  is the density of AZ61 magnesium alloy (1.8g/cm<sup>3</sup>),  $S$  is the area of samples (mm<sup>2</sup>), and  $t$  is the time of corrosion immersion test and it is 4 h for this experiments. The phase analysis was performed by D8 Advance X-ray diffract meter (XRD). Olympus optical (OM) was used to characterize the microstructure and phases of AZ61 alloy. Scanning electron microscopy (SEM) was used to exhibits the morphologies of corroded surfaces of AZ61 alloy after removal of the corrosion products.

## III. RESULTS

### A. Microstructure of AZ61-Ca alloy

The XRD pattern of as-cast AZ61 alloy is shown in Fig. 1(a). The results show that its microstructure consists of  $\alpha$ -Mg matrix,  $\text{Mg}_{17}\text{Al}_{12}$  phases. With the addition of Ca, the microstructure of AZ61+1%Ca consists of  $\alpha$ -Mg matrix,  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{Al}_2\text{Ca}$  phases as shown in Fig. 1(b). Al-Ca intermetallic compounds can be found in the alloy.

The microstructure and phases of AZ61 magnesium alloy with different content Ca addition were shown in Fig. 2. It can be obviously seen that the  $\text{Mg}_{17}\text{Al}_{12}$  phases in AZ61 magnesium alloy after solution and aging treatment were distributed in the grain interior and grain boundaries, which have granular and rod-like morphologies (see Fig. 2a). With the addition of Ca, the microstructure of AZ61 magnesium alloy was remarkably refined, and the spotted, high-melting point phase Al-Ca intermetallic compounds can be found in the alloy (Fig. 2b). A small amount of  $\text{Mg}_{17}\text{Al}_{12}$  phase remained in AZ61+1% Ca alloy also. With the increase in Ca content to 2%, a large number of blocky Al-Ca intermetallic compounds were formed and tended to segregation (Fig. 2c).

The possibility of forming metallic compounds in a casting alloy should be predicted through the electronegativity difference between two alloy elements

and the solidification kinetics during solidification. The larger the electronegativity differences between two alloy elements, the stronger the higher possibility of forming metallic compounds in alloy. The electronegativity difference between Al and Ca is higher than that between Al and Mg in this work. This means that Al-Ca compounds  $\text{Al}_2\text{Ca}$  can be formed more easily than that for Mg-Al compounds  $\text{Mg}_{17}\text{Al}_{12}$ , so  $\text{Mg}_{17}\text{Al}_{12}$  phases decrease with the addition of Ca. Blocky  $\text{Al}_2\text{Ca}$  compounds are formed. When the content of Ca exceeds 2%, the Al-Ca metallic compounds tends to segregation (see Fig. 2c), which significant affects the corrosion behavior of AZ61 alloy.

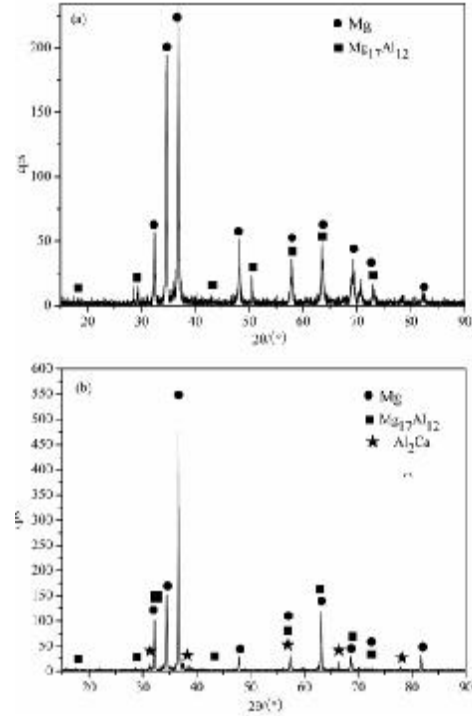


Figure 1. The XRD pattern of as-cast alloy (a) AZ61; (b) AZ61+1%Ca

### B. Corrosion behaviors of AZ61-Ca alloy

Fig.3 shows the corrosion rate of AZ61-Ca magnesium alloy at 0.1% and 3.5% NaCl solution. It can be obviously seen that AZ61 magnesium alloy shows serious corrosion in NaCl solution. And the corrosion rate of AZ61 alloy is 3.46 and 4.96 mm/a at 0.5% and 3.5% NaCl solution respectively. With the addition of different content Ca, the corrosion behavior of AZ61 alloy decreases firstly and then increases sharply. When the content of Ca is 1%, AZ61 magnesium alloy shows the lowest corrosion rate. And the corrosion rate of AZ61-1% Ca alloy is 2.19 and 2.87 mm/a at 0.5% and 3.5% NaCl solution respectively. When the content of Ca is 2%, AZ61 magnesium alloy shows the largest corrosion rate. And the corrosion rate of AZ61-2% Ca alloy is 5.34 and 9.54 mm/a at 0.5% and 3.5% NaCl solution respectively. In addition, the corrosion rates in 3.5% NaCl solution for AZ61-Ca alloy are always higher than those in 0.5% NaCl solution, indicating that NaCl concentration has a significant effect on the corrosion behavior of AZ61 magnesium alloy. The corrosion resistance of magnesium

alloy AZ61 in NaCl solution can be improved by the addition of proper content of Ca.

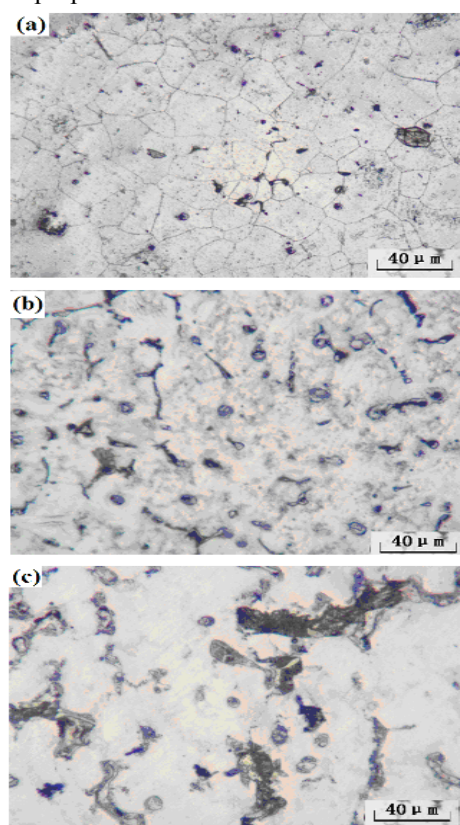


Figure 2. The microstructure of magnesium alloy (a) AZ61; (b) AZ61+1%Ca; (c) AZ61+2%Ca

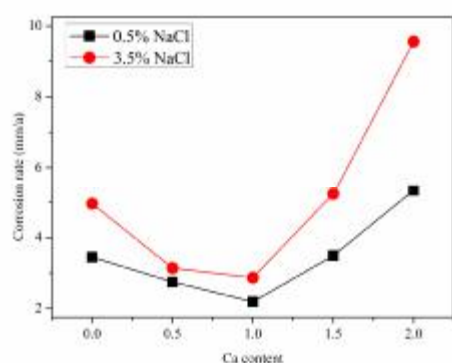


Figure 3. The corrosion rate of AZ61-Ca magnesium alloy

Fig 4 shows the morphology of corroded surfaces for AZ61 magnesium alloy with different Ca addition immersed in 3.5% NaCl solution. It can be obviously seen that many corrosion pits are observed in the corrosion surface after the separation of corrosion products for AZ61 alloy as shown Fig.4 (a). However, the corrosion surface of AZ61+1% Ca magnesium alloy very uniform and dense, which may be the reason of low corrosion rate of this alloy as shown Fig.4 (b). The AZ61+2% Ca shows serious corrosion and much large corrosion pits is formed in the surface as shown Fig.4 (c).

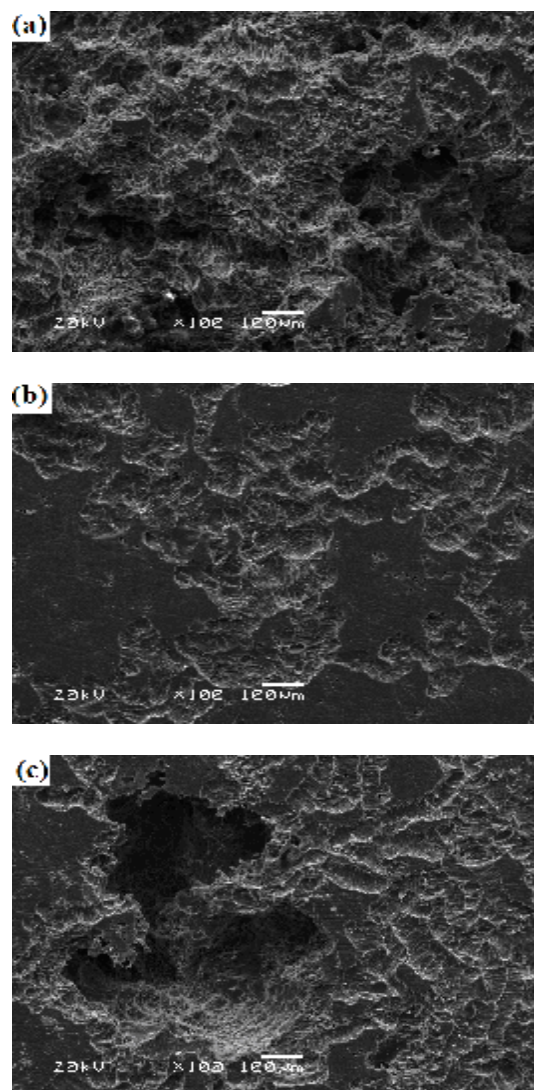


Figure 4. Morphology of AZ61-Ca magnesium alloy in 3.5%NaCl solution (a)AZ61; (b) AZ61+1% Ca; (c) AZ61+2% Ca

#### IV. CONCLUSIONS

The corrosion behaviors of AZ61 magnesium alloy with the Ca addition was researched in this paper. Based on the current results, these conclusions can be drawn as:

(1) With the addition of 0.5-2% Ca, the microstructure of AZ61 magnesium alloy is remarkably refined, and spotted, high-melting point phases Al-Ca intermetallic compounds  $Al_2Ca$  is found in the aging alloy.

(2) When the content of Ca is 1%, AZ61 magnesium alloy shows the lowest corrosion rate. And the corrosion rate of AZ61-1% Ca alloy is 2.19 and 2.87 mm/a at 0.5% and 3.5% NaCl solution respectively.

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