Research on Corrosion Resistance of Solution-treated AZ63D Magnesium Alloy

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Abstract. The as-cast AZ63D magnesium alloy and its solution-treated microstructure were examined by optical microscopy (OM) and X-ray Diffraction (XRD). The results show that the solution-treated microstructure is more even and the aggregation of β phase is decreased. The immersion testing of AZ63D magnesium alloys exposed to 3.5wt. % NaCl solution and electrochemical measurement were carried out to seek their corrosion characteristics. The results show that the corrosion weight loss of the solution-treated microstructure of AZ63D magnesium alloy is reduced by about 13.01% compared with the as-cast microstructure. The corrosion resistance of the solution-treated microstructure is obviously better than that of the as-cast microstructure. The free corrosion potential and the free corrosion current of the solution-treated microstructure is respectively about 2.70% higher and 6.83% less than that of the as-cast microstructure.

1. Introduction

As a light material, AZ63 magnesium alloy has many good properties, and it has been used in transportation. It is regarded as one of the most promising materials for the near future. However, their further application is limited by its poor corrosion resistance. Therefore improvement of its corrosion resistance is an urgent problem.

In recent decades, a great number of researchers have carried out a considerable amount of work on the corrosion of AZ63 magnesium alloy. They have studied part of corrosion resistance and factors influencing it [1-3]. Different corrosion conditions were studied systematically to summarize different effects of environmental and metallurgical factors on corrosion of magnesium alloys [4-6]. The amount of precipitate in AZ63 magnesium alloy changes indistinctively with the temperature changing, so till now it is hardly reported that the systematic researches on improving the corrosion resistance of AZ63 magnesium alloy with the change of its microstructure by heat treatment. In fact, appropriate heat-treatment can regulate precipitate and distribution of composition, which evidently affects the corrosion resistance of AZ63 magnesium alloy. Besides, flux with chloride ion must be used during preliminary smelting and succeeding refining of magnesium and its alloys in the metallurgical industry at present and it is difficult to remove the contamination of chloride ion in the process of production, storage and transportation, so it is especially meaningful to research on the corrosion-resistance of different AZ63 magnesium alloy microstructures in electrolyte solution.
The research aims at broadening the thinking of research on the corrosion resistance of AZ63D magnesium alloy, seeking the corrosion mechanism of the alloy in electrolyte solution, and providing theoretical and testing basis for more extensive application of the alloy.

2. Experimental procedure

The theas-cast AZ63D magnesium rods were made by four steps. (1) Oil and oxide layer on the surface of pure magnesium (99.98wt. %), pure aluminium (99.9wt. %), pure Zn (99.9wt. %) and aluminium-manganese master alloy were cleaned out. They were preheated to 150 °C. (2) The preheated magnesium ingot was put into a graphite crucible, which has been heated to 500 °C. Meanwhile, high purity argon was input and then the temperature was risen to 770 °C. (3) A certain proportion of pure aluminum, pure Zn and aluminium-manganese master alloy were added to the molten melt. When the solid phases were melted absolutely, refining agent was added into the melt. It was stirred for 25min and stood for 20min. Then, the melt was cooled to 720 °C. (4) The melt was rapidly poured into the tube-shaped steel mold (outer diameter: 50mm, inner diameter: 35mm, height: 300mm) and the theas-cast AZ63D magnesium alloy rods with a size of 35mm in diameter were got.

The chemical composition of the theas-cast AZ63D magnesium alloy is listed in Table 1.

| Table 1. Chemical composition of the theas-cast AZ63D magnesium alloy (wt. %) |
|-------------------|---|---|---|---|---|---|---|
| Mg | Al | Zn | Mn | Si≤ | Fe≤ | Cu≤ | Ni≤ |
| Bal. | 5.52 | 2.94 | 2.94 | 0.8 | 0.003 | 0.01 | 0.001 |

Part of the theas-cast AZ63D magnesium alloy rods were solution-treated (T4) by vacuum resistance furnace. The process was as follows: heating to 360 °C continuously and holding for 3h, then heating to 420 °C and hold for 17h. cool the alloy in air eventually.

Theas-cast AZ63D magnesium alloy rods and solution-treated rods were cut to make specimens. X-ray diffraction (XRD, model 7000) was performed on the bulk specimens to confirm phases. The main test conditions were using incident rays (Cu target, ϵKα1) of 1.5406 Å and accelerating voltage of 8.0 kV. The morphologies were characterized using optical microscopy (OM, model XJZ-6A).

The weight loss were measured according to the procedure of ASTMG-1-72. The work area of AZ63D magnesium alloy was 86.55mm² and non-work area was sealed with epoxy resin. All the specimens were initially cleaned following the procedure of ASTM standard. The specimens were polished to be smooth and cleaned using anhydrous ethanol and distilled water. Afterwards, they were dried by cold wind and pre-weighed by analytical balance (model TG328A, precision 0.01mg). The polished and pre-weighed specimens were exposed to the 3.5%NaCl solution (1000 ml) for 10h totally and they were weighed per hour. Before the specimens were weighed, they were scrubbed for 3min with 180g·L⁻¹ CrO₃ solution to remove oxide and corrosion products and then cleaned again using anhydrous ethanol and distilled water.

Electrochemical polarization experiments were carried out using an Auto Lab Corrosion measurement system. A standard three-electrode configuration was adopted. The exposed area was 87.50mm². The specimens were given a metallographic polishing prior to each experiment, followed by washing with distilled water and anhydrous ethanol, and then dried. Specimens were immersed in the 3.5wt.% NaCl solution, and a polarization scan was carried out at a rate of 10 mVs⁻¹ and over a polarization potential range from -1.7V to + 1.0V, after allowing a steady state potential to develop.
3. Results and discussion

3.1. Microstructure of the as-cast and solution-treated AZ63D magnesium alloy

3.1.1. Microstructure of the as-cast AZ63D magnesium alloy. The phase of the as-cast AZ63D magnesium alloy is as shown in its XRD spectrum (Fig. 1). We can know that its phase consists of solid solution $\alpha$-Mg and $\beta$-Mg$_{17}$Al$_{12}$ phase.

![Figure 1. XRD spectrum of the as-cast AZ63D magnesium alloy](image)

Fig. 2 shows microstructure of the as-cast AZ63D magnesium alloy. Refering to XRD pattern, obviously, the black precipitates near the boundary and the interior of the crystallized $\alpha$-Mg phase are $\beta$-Mg$_{17}$Al$_{12}$ phase, which is formed by non-equilibrium solidification. There may also be a small number of Zn element in the $\beta$-Mg$_{17}$Al$_{12}$ phase, which is because of the high Zn element existing inside of AZ63D.

![Figure 2. Microstructure of the as-cast AZ63D magnesium alloy](image)

3.1.2. Microstructure of the solution-treated AZ63D magnesium alloy. XRD spectrum of the solution-treated AZ63D magnesium alloy (T4) is given in fig. 3. It reveals that the solution-treated AZ63D magnesium alloy almost consists of $\alpha$-Mg phase, and $\beta$-Mg$_{17}$Al$_{12}$ phase is almost dissolved by solution treatment.
Fig. 4 shows the microstructure of the solution-treated AZ63D magnesium alloy. It can be seen that the microstructure of solution-treated AZ63D magnesium alloy is relatively even. Compared with the as-cast microstructure, these grains have obvious growing trend. The corroded black spots can still be observed at the interior of grains. The reason is that though the alloy is cooled fast, there is still a small amount of $\beta$ phase precipitating from the microstructure. $\beta$ phase can't be detected by XRD pattern and this is because that the amount of it is too small.

Figure 4. Microstructure of the solution-treated AZ63D magnesium alloy

3.2. Corrosion resistance of the AZ63D magnesium alloy

3.2.1. Immersion testing. Fig. 5 shows the curve of corrosion weight losses of the as-cast and solution-treated AZ63D magnesium alloy in the 3.5wt. % NaCl solution. Obviously, as the time goes on, the degree of corrosion of both tend to aggravate. The trend of corrosion weight loss of solution-treated microstructure is similar to that of as-cast structure. However, the corrosion weight loss of the solution-treated microstructure of AZ63D magnesium alloy is reduced by about 13.01% compared with the as-cast microstructure. This is because that the solution-treated microstructure becomes more even, which reduces content of the $\beta$ phase and galvanic corrosion. Thus the corrosion resistance of AZ63D magnesium alloys can be promoted.

Figure 5. Curve of corrosion weight losses of the as-cast and solution-treated AZ63D magnesium alloy in the 3.5wt. % NaCl solution
3.2.2. Electrochemical testing. Fig. 6 shows the potentiodynamic polarization curves for the theas-cast and solution-treated AZ63D magnesium alloy in 3.5 wt. % NaCl solution. It can be inferred that the characteristic of polarizational corrosion of the solution-treated AZ63D magnesium alloy is similar to that of the theas-cast AZ63D magnesium alloy in 3.5 wt. % NaCl solution. Their pitting potentials ($E_{pt}$) are lower than the free corrosion potentials ($E_{corr}$), which means that both AZ63D magnesium alloy can be corroded spontaneously in 3.5 wt. % NaCl solution. Additionally, the free corrosion potential of the solution-treated AZ63D magnesium alloy is about 2.70% higher than that of the theas-cast alloy, and its free corrosion current is about 6.83% lower than that of the theas-cast alloy. Therefore, the corrosion resistance of theas-cast AZ63D magnesium alloy can be promoted by solution treatment effectively.

![Figure 6. Potentiodynamic polarization curves for the theas-cast and solution-treated AZ63D magnesium alloy in 3.5 wt. % NaCl solution](image)

4. Conclusion
Microstructure observations and corrosion tests of the theas-cast and solution-treated specimens of AZ63D magnesium alloy were finished and the conclusions are as follows:

1. The microstructure test shows that the microstructure of theas-cast AZ63D magnesium alloy has $\beta$-Mg$_{17}$Al$_{12}$ phase near the boundary and the interior of the crystallized $\alpha$-Mg phase, which is formed by non-equilibrium solidification. The microstructure of the solution-treated AZ63D magnesium alloy is relatively even compared with that of the theas-cast AZ63D magnesium alloy. These grains have obvious growing trend and there is a small amount of $\beta$-Mg$_{17}$Al$_{12}$ phase precipitating from the interior of grains.

2. The corrosion test in 3.5 wt. % NaCl solution shows that the corrosion weight loss of the solution-treated microstructure of AZ63D magnesium alloy is reduced by about 13.01% compared with the theas-cast microstructure.

3. The dynamic potential polarization curves for the theas-cast and solution-treated AZ63D magnesium alloy in 3.5 wt. % NaCl solution show that the corrosion resistance of the solution-treated microstructure is obviously better than that of the theas-cast structure. The free corrosion potential and the free corrosion current of the solution-treated microstructure is respectively about 2.70% higher and 6.83% lower than that of the theas-cast microstructure.

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