Corrosion and electrochemical behavior of as-cast Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloys in 5% NaCl aqueous solution

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Abstract: The corrosion mechanism of the as-cast Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloy immersed in 5% NaCl aqueous solution was investigated by electrochemical test and SEM. The electrochemical results indicate that the corrosion resistance of Mg-5Y-7Gd-1Nd-0.5Zr alloy in 5% NaCl aqueous solution gradually deteriorates with immersion time increasing from 2 h, 24 h, 60 h, to 108 h, which is consistent with the SEM observation of corrosion morphologies. The Cl\(^{-}\) anion leads to the initiation and development of the corrosion pits, and Mg-5Y-7Gd-1Nd-0.5Zr alloy exhibits filiform type of attack under significant anodic control of magnesium solution reaction. The corrosion potential becomes noble with increasing immersion time.

Key words: magnesium alloys; Mg-5Y-7Gd-1Nd-0.5Zr; corrosion; electrochemical behavior

1 Introduction

Due to their low density and high strength/mass ratio, magnesium alloy offers various possibilities as regards applications in the automotive and aeronautical industries, which is regarded as the green and promising materials of the 21st century [1–3]. In recent years there has been a rapid growth in the development of high strength, light mass magnesium alloys for elevated temperature applications. Among their usage limitations, their poor resistance to aqueous corrosion has to be taken into account [4–6].

Magnesium alloys containing heavy rare earth elements are becoming more and more attractive due to their high strength and ductility [7–10]. They have large potential applications as light structural materials for the aerospace and racing automotive industries. It is well known that the addition of rare earth (RE) elements is an effective way to improve the mechanical properties of magnesium. The corrosion behavior of magnesium alloy with RE element has been investigated. The Mg-RE-Zr magnesium alloy system, which usually contains Y, Nd, Gd and some other rare-earth elements, is the most successful magnesium alloys in this category at present, with examples as WE43 [11], WE54 [12], Mg-5Y-7Gd-1Nd-0.5Zr [13]. In the Mg-RE-Zr magnesium alloy system, Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloy is invented by our laboratory, which is used widely in the aeronautics and aeronautics. The excellent performance of Mg-5Y-7Gd-1Nd-0.5Zr alloy was achieved in industrialized tests and met the requirement of industrial productions, which set a foundation for the industrial application of Mg-Y-RE-Zr magnesium alloys. LI et al [14] found that hot extrusion experiments indicate that both the strength and plastic are improved with increasing the extrusion ratio; when the extrusion ratio is more than 20:1, the effect of grain refinement strengthening have a little improvement.

As for the corrosion behaviour of the Mg-RE-Zr magnesium alloy system, there are several investigation on them [15–16], and they present better anti-corrosion
property than the Mg-Al, Mg-Mn and other magnesium alloy system. Guo investigated the corrosion behavior of Mg-6Gd-3Y-0.4Zr alloy in NaCl solutions. They found that the corrosion products formed in 5.0% (mass fraction) NaCl solution were mainly Mg(OH)₂ and Gd(OH)₃. The improved corrosion resistance was attributed to the heat treatment and addition of heavy rare earth element [17]. However, the content of RE has significant effect on the mechanical property and corrosion behavior. TAKENAKE and his group produced magnesium metals containing rare earth elements (La, Ce and Nd). The corrosion resistance was improved greatly by a small content of RE, whereas the excess addition of RE deteriorated the corrosion resistance [18].

In this study, the basal corrosion behavior of as-cast Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloy in 5% NaCl aqueous solution was investigated at ambient temperature. The objectives of this study are to investigate the corrosion mechanism and electrochemical behavior of the Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloy in NaCl aqueous solutions.

2 Experimental

2.1 Test materials

The magnesium alloy used yttrium, neodymium, gadolinium, and Mg-30Zr master alloys as the raw materials to prepare the Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloys. All the alloys were melted in a mild steel crucible with the protection of homemade flux. When the fused mass temperature reached 1 023 K, the yttrium, neodymium, and gadolinium were added into the crucible, and then the temperature was raised to 1 123 K and kept for 20 min. Finally, the Mg-30Zr master alloys were put into the molten metals and stirred for 5 min, and then poured into a steel mold with a diameter of 98 mm [14]. Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloys used in this study were prepared by ingot casting process according to industrial casting norm specimens with the dimension of 10 mm×10 mm×10 mm, were used for all the experiments. The actual compositions of the Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloys studied were determined by Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES), and the results of the alloy are listed in Table 1. And the XRD pattern of the as-cast Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloy was studied by LI [14], and the XRD pattern was shown in Fig. 1. It can be seen from Fig. 1 that the Mg-RE phases of the as-cast Mg-5Y-7Gd-1Nd-0.5Zr magnesium alloys are Mg₂₅Y₅, Mg₄₁Nd₅ and Mg₇Gd.

| Table 1 Nominal composition of Mg-5Y-7Gd-1Nd-0.5Zr alloy (mass fraction, %) |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Y               | Gd              | Nd              | Zr              | Mg              |
| 4.53            | 7.04            | 1.29            | 0.49            | Bal.            |

2.2 Immersion test

The specimens for the immersion test were 10 mm×10 mm×10 mm in size. Before the test, the specimens were polished with SiC abrasive papers from P120 to P2000, and cleaned with acetone and de-ionized water. Every specimen was weighed (original mass, m₀) and the surface area (S) was measured before the test. The corrosion media were 5% NaCl aqueous solution opened to the air at about 25 °C. The samples were immersed in the three solutions for 0 h, 2 h, 24 h, 60 h and 108 h. After each immersion test, the corrosion products of the specimens in the experiment were cleaned by dipping in a 400 mL aqueous solution of 10% CrO₃+1% AgNO₃ for 5 min in boiling condition. The specimens were then quickly washed with de-ionized water and dried again, and weighed the final mass (m₁). The difference between m₀ and m₁ was designated as the corrosion mass loss.

2.3 Preparation and surface characterization

For metallographic characterization, samples were wet ground through successive grades of silicon carbide abrasive papers from P120 to P2000 followed by diamond finishing to 0.1 μm, followed by rinsing with isopropyl alcohol in an ultrasonic bath and drying in warm air. In all cases, the tests were performed in duplicate to guarantee the reliability of the results. JSM−6510A analytical scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS) was used to observe the corrosion morphologies and analyze the elements. The specimens for SEM were revealed by 4% nitric acid in alcohol.
2.4 Electrochemical measurements

Potentiodynamic is a conventional method in which the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. The evaluation of polarization curves is often used in corrosion studies to obtain some kinetic information on the overall corrosion reaction like the corrosion potential ($\phi_{corr}$) and the corrosion current density ($J_{corr}$). The samples for electrochemical measurement were molded into epoxy resin with only one side exposed as working surface available. The corrosive medium was 5% NaCl aqueous solution (pH 6.1 in contact with air at about 20 °C. The samples were immersed in 5% NaCl aqueous solution for 2 h, 24 h, 60 h and 108 h at free corrosion potential.

Electrochemical measurements were performed using specimens of working area 1cm\(^2\) immersed in 5% NaCl at room temperature ((22±1) °C). An potentiator/Galvanostat Model 273A connected to a three-electrode cell was used for the electrochemical measurements; the working electrode was the test material, the counter electrode was Pt and the reference electrode was saturated calomel electrode (SCE) with a potential of 0.197 V with respect to the standard hydrogen electrode. Polarization measurements were carried out at a scan rate of 0.3 mV/s, from −100 mV to +400 mV with respect to the corrosion potential ($\phi_{corr}$). The anodic corrosion current density was limited to 5 mA/cm\(^2\).

3 Results and discussion

3.1 Corrosion morphologies of Mg-5Y-7Gd-1Nd-0.5Zr ingots

Few of hydrogen bubbles gradually presented on the surface of the Mg-5Y-7Gd-1Nd-0.5Zr alloys at the initial time, soon afterwards the number of hydrogen bubbles got to accelerate. After the specimens immersed in 5% NaCl aqueous solution for 2h, pitting corrosion presented on the surface of the specimens. In the 5% NaCl aqueous solution, the Cl\(^-\) anion could destroy the oxide/hydroxide film formed on the surface of the magnesium alloy and thus caused the initiation of the pitting corrosion [19]. Figure 2 shows the corrosion morphologies of the Mg-5Y-7Gd-1Nd-0.5Zr specimen surfaces immersed in 5% NaCl aqueous solution for 2 h where the corrosion products has been removed. The corrosion initiates from a few small pitting and enlarges gradually and new pitting occurs subsequently, as shown in Fig. 2(a). Figures 2(b)–(c) are the magnified morphologies of Fig. 2(a). Clear filiform corrosion morphology was also observed after immersion for 2h as shown in Fig. 1(a). The corrosion tracks appeared filament feature. The filiform corrosion began from the black corrosion sites and then spread toward Mg-RE phase. There was a white netted phase around almost every dent, as shown Fig. 2(c). In fact, the formation of the corrosion pits and dents was closely related to the microstructure of the magnesium alloy. Comparing with the Mg-RE phases (Mg\(_{24}\)Y\(_5\), Mg\(_{41}\)Nd\(_5\) and Mg,Gd), the primary $\alpha$-Mg phase was easily corroded and fall off from the corroded alloy surface. An EDS analysis for this phase indicates that the percentage of RE was higher than that in the dent, which means the white phase was the Mg-RE and the dent was likely the primary $\alpha$-Mg phase. The reason for the formation of the dents was that the corrosion resistance of the $\alpha$-Mg phase is worse than that of the hypo-eutectic...
Mg-RE phase, so that the $\alpha$-Mg dissolved sooner than the eutectics and ultimately a dent left. There was still some $\alpha$-Mg phase left on the specimen surface, which implied that the corrosion rate of the specimen immersed in the NaCl solution was possibly quite slow. When $\alpha$-Mg around the Mg-RE phases was corroded out, the $\alpha$-Mg connected Mg-RE phases also fall off. The reduction of the second phases caused the reduction of the cathodic fraction on the surface, finally leading to the reduction of corrosion rate. The thin film formed on the Mg-5Y-7Gd-1Nd-0.5Zr in the initial stage of immersion did not show excellent protection to the alloy.

Figure 3 shows the surface features of Mg-5Y-7Gd-1Nd-0.5Zr specimens after removing the corrosion products, which were exposed to 5% NaCl aqueous solution for 24 h, 60 h and 108 h. The distributions and size of the dents on the three specimen surfaces got further aggravated. Comparing Fig. 3(a) with Fig. 3(b) and Fig. 3(c), the dents on the surface of the specimen immersed in the solution appear much deeper with increasing exposure time. The corrosion morphologies of Mg-5Y-7Gd-1Nd-0.5Zr alloy with various exposure times prove that the second phases play an important role in accelerating the corrosion of $\alpha$ Mg matrix. When Mg-5Y-7Gd-1Nd-0.5Zr alloy was immersed in NaCl solution for 24 h as shown in Fig. 3(a), the filiform attacks got further aggravated. The surface was covered with a large number of corrosion filaments, resulting in that the tracks of corrosion filaments were difficult to be identified and the corrosion pits continued to grow in depth direction. The filiform corrosion initiated from a central site, and then some filaments diverged toward different direction. Most of the filaments were not perfectly straight, but there also appeared to be some symmetry in the way they wiggled. The tracks never crossed each other. If a filament encountered another filament, it would terminate or reverse toward other direction to grow. The corrosion filament would finally extinct with decreasing of the remaining space [20].

![Fig. 3 SEM morphologies of specimens after removing corrosion products on specimen surfaces immersed for 24 h (a), 60 h (b) and 108 h (c, d, e) in 5% NaCl aqueous solution](image-url)
There were some second phases embedded in the wall of corrosion pits as shown in Fig. 3(e), which played an important role in accelerating the corrosion of $\alpha$-Mg matrix with increasing exposure time. The primary $\alpha$-Mg phase was the main objects which suffered from the worse corrosion. Thus, the second phases would act as long-term cathodic phases to accelerate the corrosion of Mg-5Y-7Gd-1Nd-0.5Zr alloy. SEM image of the second phase as shown by the arrows in the corrosion pit (Fig. 3(d) and Fig. 3(e)) was magnified Fig. 3(c). It is found that the $\alpha$ Mg matrix surrounding the second phase is depleted due to corrosion, but the second phase still keeps intact and protrudes from the matrix surface. This result proves that the second phases act as strong cathodes and the $\alpha$-Mg matrix surrounding the second phases acts as anode during the corrosion process.

The EDS spectrum and the chemistry compositions of Mg-5Y-7Gd-1Nd-0.5Zr alloys after removing the corrosion products are shown in Fig. 4. The quantities of the chemistry compositions for the Mg-5Y-7Gd-1Nd-0.5Zr after removing the corrosion products are almost the same as that of the original surface. The distributions of the chemistry compositions indicated that the noble second phase particles are mainly compounds of Mg, Y, Gd, Nd and their hydroxide.

![Fig. 4 SEM image (a) and EDS results (b) of surface of Mg-5Y-7Gd-1Nd-0.5Zr alloy after removing corrosion products](image-url)

### 3.2 Corrosion mass loss rate and corrosion product thickness

The corrosion mass loss rate of the specimen was calculated as follows:

$$v = \frac{(m_0 - m_1)}{St}$$

where $m_0$ is the original mass, g; $m_1$ is the final mass without the corrosion products, g; $S$ is the surface area cm$^2$; $t$ was the immersion time, h.

Figure 5 show the relationship between the corrosion mass loss rate and the immersion time. The corrosion mass loss rate tended to continuously increase within the testing time because of the continuously increase of the corrosion depth and corrosion pits, which significantly increased the corrosive area and thus enhanced the corrosion rate [21]. In the initial stage, the corrosion mass loss rate was very small. When the immersion time was less than 24 h, the corrosion weight loss rate in the solutions increased quickly, but the corrosion weight loss rate decreased sharply when immersed for more than 24 h.

![Fig. 5 Corrosion mass loss rate for as-cast Mg-5Y-7Gd-1Nd-0.5Zr alloy immersed for different times in 5% NaCl solutions](image-url)

### 3.3 Electrochemical measurements

#### 3.3.1 Open Circuit Potential

The open circuit potential (OCP) experiments were carried out in 5% NaCl solution with saturated Mg(OH)$_2$ and the results were showed in Fig. 6, which disclosed the variation of electrode potential with immersion time. Two principle regularities could be gotten from those curves. First, the curve of Mg-5Y-7Gd-1Nd-0.5Zr sample could be divided into two stages. The corrosion potential of Mg-5Y-7Gd-1Nd-0.5Zr increased to the highest one quickly in the initial several seconds as soon as they were immersed into the solution, then increased quickly. After reaching the bottom values, the curve of the Mg-5Y-7Gd-1Nd-0.5Zr sample fell up slightly with little...
fluctuation. The value of the open circuit potential kept rapidly moving up and down at \(-1.658 \text{ V}\) during the period of immersion time after 20 min. Some pits were formed and hydrogen bubbles were evolved from the pits. Second, during the exposure time, pure Mg whose corrosion potential is \(-1.790 \text{ V}\) \([22]\) showed a more positive corrosion potential than Mg-5Y-7Gd-1Nd-0.5Zr. ZENG et al \([23]\) also found that the corrosion potentials of Mg-RE alloys (Mg-Gd, Mg-Dy, Mg-Nd-Zr, Mg-Gd-Nd-Zr and Mg-Dy-Nd-Zr) were more negative than that of pure Mg in 5% NaCl solution saturated with Mg(OH)\(_2\). It has been reported that rare earth element could enrich on the surface, and modify the surface film of magnesium alloy \([24]\). For instance, the pseudo-passivation occurred in rapidly solidified Mg-Y alloys. However, the potential of Mg-5Y-7Gd-1Nd-0.5Zr alloy decreased drastically after 20 min and then fluctuates between \(-1.648\) and \(-1.661 \text{ mV}\), and stabilized at \(-1.658 \text{ mV}\) finally. This was caused by the fact that magnesium was easily oxidized to form a thick oxide/hydroxide film when it came into contact with humid air or water \([25]\). The drop in potential after 20 min exhibited that the oxide film reacted quickly with water and forms magnesium hydroxide as shown in Eq. (2):

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2
\]

After the dissolution of MgO, the magnesium substrate would continue to react with the media and the magnesium hydroxide was produced and hydrogen gas evolves:

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2 \uparrow
\]

The big undulation of Mg-5Y-7Gd-1Nd-0.5Zr in \(\varphi_{\text{corr}}\) reflected the formation and breakdown of partially protective film Mg(OH)\(_2\).

### 3.3.2 Potentio-dynamic polarization

A cyclic polarization curve could indicate the tendency of a material to undergo pitting in a specific corrosion environment. The technique was particularly useful in the development of alloys with high pitting resistance \([26]\). Figure 7 presents the cyclic polarization curves for Mg-5Y-7Gd-1Nd-0.5Zr after immersion in 5% NaCl solution saturated with Mg(OH)\(_2\) for 0, 24, 60, and 108 h. Generally, the cathodic polarization curves were assumed to represent the cathodic hydrogen evolution, whilst the anodic curves represented the dissolution of magnesium. All specimens revealed an obvious shift of \(\varphi_{\text{corr}}\) toward more noble value and a decrease of passive current density with increasing immersion time. It might be due to the nucleation and growth of a thick and semiprotective layer of corrosion products reported by PARDO et al \([27]\). With increasing immersion time, the corrosion film got thicker and thicker, which provided the alloy with an protective effect. The thick corrosion film presented a protective effect of the Mg-5Y-7Gd-1Nd-0.5Zr alloy. The current density increased quickly after the electrode potential after exceeding the corrosion potential. This was attributed to the difference between the \(\alpha\)-Mg and the second phase and the lower compactness of corrosion product film on the Mg-5Y-7Gd-1Nd-0.5Zr alloy. According to the study of HARA et al \([28]\), the corrosion product films formed on the Mg alloys during the open-circuit immersion were protective and led to spontaneous passivation. When the electrode potential exceeded a critical value (pitting potential), the current density began to increase sharply. This increase in current density was followed by the evolution of hydrogen on the electrode surface, and the corrosion film suffered local breakdown \([26]\).

Comparing with the pure Mg whose \(\varphi_{\text{corr}}\) is \(-1.790 \text{ V}\), the \(\varphi_{\text{corr}}\) of the Mg-5Y-7Gd-1Nd-0.5Zr with different immersion times are higher than \(-1.658 \text{ V}\). It can be
concluded that the presence of the rare earth elements in the corrosion product film has been thought to increase the corrosion resistance of the alloy [29–30]. KRISHNAMURTHY et al [31] noted a pseudo-passivation behaviour in rapidly solidified binary Mg-(10%–26%)Nd alloy; the pseudo-passivation was attributed to Nd enrichment in the corrosion product film. NORDIEN et al [32] found that the presence of RE elements caused a significant reduction in film hydration and improved the passive properties of the corrosion film. NAKATSUGAWA et al [33] have reported that the addition of heavy rare earth elements is effective in suppressing Mg corrosion. Maybe the corrosion rate of the Mg-5Y-7Gd-1Nd-0.5Zr alloy can be slightly reduced by the rare earth.

4 Conclusions

1) The existence of the Cl− anion in the immersion circumstance led to the initiation and development of the corrosion pits, and the corrosion pits led to the corrosion dents and even the corrosion areas.

2) The corrosion presented the clear filiform corrosion morphologies in the initial corrosion time, and the corrosion rates were as follows: slow, quick, slow with increasing immersion time, which could be obtained from the corrosion morphologies and the corrosion weight loss rate.

3) The value of corrosion potential of Mg-5Y-7Gd-1Nd-0.5Zr was −1.658 V(vs SCE) and was approximately 132 mV higher than that of the pure magnesium. With increasing immersion time, the corrosion potential obviously increased, but the passive current density decreased because of the nucleation and growth of a thick and protective layer of corrosion products.

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References


