Effect of aging treatment on corrosion behavior of Mg-4Nd-2Gd-0.5Zr alloy

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Abstract

The effects of aging time on corrosion behavior of Mg-4Nd-2Gd-0.5Zr alloy in 3.5% NaCl solution were investigated by microanalysis, weight loss test and electrochemical test. The results show that the corrosion rate of Mg-4Nd-2Gd-0.5Zr alloy decreases first and then increases with the extension of aging time. Aging treatment alters the grain size and the distribution of the second phases. The second phases and grain size are the key factors affecting the corrosion rate of magnesium alloy. Among the tested alloys, the T6-8 h alloy shows the lowest corrosion rate, which is mainly attributed to the continuous distribution of second phases restricting the expansion of corrosion, hence the T6-8 h alloy showed the highest corrosion resistance. The corrosion rate of T6-16 h alloy increases obviously because of the growth of the grain size and the segregation of second phases, which accelerates the corrosion progress.

1. Introduction

Among the structure metal materials, magnesium alloy has been widely used in automobile industry, electronics, aerospace and other fields because of its excellent specific stiffness and specific strength, but low strength and poor corrosion resistance limit the wider application of magnesium alloy. Adding rare earth elements to pure magnesium can improve the microstructure, fine grain size and remove S, Fe and other impurities, so RE elements can effectively improve the mechanical properties and corrosion resistance of magnesium alloy [1–3]. RE element can also change the structure of corrosion film of magnesium alloy. Zhou et al. [4] found that the corrosion product film of AM60 magnesium alloy was denser with the addition of Nd, which could block the penetration of Cl⁻, thus improving the corrosion resistance. Wang et al. [5] had studied Mg-Nd binary alloy, and found that the as-cast microstructure of Mg-4Nd alloy is composed of α-Mg matrix and intermetallic compound Mg₈₁₂Nd phase, the distribution of Mg₁₂Nd with high hardness at grain boundaries effectively improves the strength of alloy. The solubility of Gd in magnesium is sensitive to temperature and can produce satisfactory heat treatment strengthening effect. Luo and Chen et al. [6–8] found that the compound of Gd and Nd in magnesium can decrease the solubility of each other and improve the precipitation strengthening effect. Zr element usually exists as a grain refiner in magnesium without Al and Mn [9, 10] elements. Tong et al. [11, 12] studied the effect of Zr on the corrosion resistance of magnesium alloy and found that add 0.5 wt% Zr to magnesium alloy can improve the corrosion resistance of the alloy. Wang et al. [13] added 0.7 wt% Zr to Mg-4Nd alloy, the tensile strength of alloy increased by about 25% to 267 MPa after extrusion and T6 treatment, which makes Mg-Nd-Zr alloy has a greater prospect of industrial application. In this paper, 2 wt% Gd was added to Mg-4Nd-0.5Zr alloy to increase precipitation strengthening effect, and Mg-4Nd-2Gd-0.5Zr alloy was selected as the research object to study the effect of aging treatment on corrosion resistance.

Magnesium has the lowest electrode potential in all structure materials [14–16]. Therefore, magnesium alloy has strong anodization in seawater and is easily damaged by corrosion as anode in galvanic corrosion, which
limits the application of magnesium alloy. Heat treatment is a commonly used strengthening method for Mg-RE alloy [17–19], but the effect of heat treatment on the corrosion behavior of Mg-RE alloy has not been unified. Dinh et al. [20–23] reported that the solid solution treatment can eliminate the composition segregation, so that most of second phases formed during solidification were dissolved in the matrix, and the amount of galvanic corrosion was reduced, thus improving the corrosion resistance. However, the effect of aging treatment on the corrosion resistance of solid solution alloy varies with different alloy systems. Li et al. [24–28] reported that aging treatment increased the numbers of cathodes in the galvanic corrosion and decreased the corrosion resistance of the solid solution alloy, but the results of the study on magnesium alloys by Gui et al. [29–31] showed that appropriate aging treatment changed the distribution of second phase and increased the protective effect of second phase, and hence enhances the corrosion resistance.

In practical production and application, the corrosion resistance of magnesium alloys is an important factor restricting their wide application. Therefore, it is of great significance to study the corrosion behavior of magnesium alloy. Solid solution and aging treatment improve the strength of Mg-4Nd-2Gd-0.5Zr alloy, this improves the possibility of industrial application of Mg-Nd-Gd-Zr alloy. However, little attentions have been paid to the effect of aging treatment on the corrosion behavior of Mg-Nd-Gd alloy, it is necessary to clarify the effect of aging process on the corrosion behavior of Mg-4Nd-2Gd-0.5Zr alloy. This paper investigates the corrosion behaviors of Mg-4Nd-2Gd-0.5Zr alloys under different aging treatment process, analyzing and discussing the corrosion mechanism of Mg-4Nd-2Gd-0.5Zr alloy in NaCl solution. This paper expects to provide data reference for development of Mg-Nd-Gd alloys with excellent strength and favourable corrosion resistance.

2. Experiment

2.1. Preparation of test materials

The raw materials used for this experiment were pure magnesium (≥99.8%), Mg-30 Nd (mass percent, the same below), Mg-30 Gd, Mg-30 Zr master alloy. All raw materials need to be ground off the surface oxide film and dried before melting. The smelting was in the electromagnetic induction furnace. All raw materials were heated to 750 °C until all materials melt, let stand for 5 min. In melting process, a mixture gas of CO₂ + SF₆ (volume ratio, 99:1) was continuously injected to create a protective atmosphere. Finally, the alloy liquid were poured into the permanent mold that had been preheated at 250 °C, and the alloy ingot of nominal composition is Mg-4Nd-2Gd-0.5Zr was got. According to the previous research results [21], the heat treatment process of the alloy is solution (525 °C for 8 h) + aging (225 °C for different time) treatment. The solution treatment was carried out in the box resistance furnace, as-cast alloy was kept in 525 °C for 8 h and then quenched in 80 °C water, named T4. Aging treatment was carried out in the electric heating blast drying oven, in the previous study [21], Mg-4Nd-2Gd-0.5Zr alloy reached peak-aged hardness after aged for 8 h, and the microstructure showed over-aged characteristics (grain and the second phase coarsening) at 16 h. Therefore, in order to study the effect of different aging time on the alloy, the T4 samples were aged at 225 °C for 4 h, 8 h (peak-aged), 12 h and 16 h (over-aged) respectively in this experiment, and named T6-4 h, T6-8 h, T6-12 h, T6-16 h accordingly. The alloys in various states were cut into 10 mm × 10 mm × 10 mm cubic specimen by wire cutting equipment for subsequent experiments.

2.2. Experimental steps and analysis methods

All surfaces of the cubic specimen that was used for weight loss test were ground on 800#, 1200#, 2000# sandpapers, then the specimens were cleaned with anhydrous alcohol and dried. After drying, the dimensions of the specimens were measured, and weighting the specimens by electronic balance. The corrosion medium is NaCl aqueous solution with a mass concentration of 3.5%, the test temperature is room temperature, and test time is one day. After immersion test, the specimens were put into boiled chromic acid (200 g/l CrO₃, 10 g/l AgNO₃) to remove corrosion products, and then cleaned and weighed. The average corrosion rate is calculated by the following formula [32]:

\[
P_W = \frac{2.10 \Delta W}{At}
\]

where: \(P_W\) is the corrosion rate, mm y⁻¹; \(\Delta W\) is the specimen weight loss, mg; \(A\) is the exposes surface area of specimen, cm²; \(t\) is immersion time, day.

The samples for electrochemical are 10 mm × 10 mm × 10 mm cubic specimens. The alloy specimens were ground on 2000# sandpaper to rub off the surface oxide film before electrochemical test, polishing one surface (10 mm × 10 mm) as the working surface. Then the specimens were connected with copper wire and encapsulated surfaces with denture powder except for the working surface. Electrochemical equipment is CHI660D electrochemical workstation, test temperature was room temperature, and electrolyte was 3.5% NaCl solution.
aqueous solution. This test used a three electrode system, of which specimens were working electrode, graphite electrode was counter electrode, and reference electrode was saturated calomel electrode. Firstly, soaking the working electrode in electrolyte for 20 min until the open circuit potential was stabilized. After the potential of the working electrode was stable, electrochemical impedance spectroscopy (EIS) was measured under the stable open circuit potentials. The frequency scanning range was 100 kHz to 0.1 Hz, the excitation signal amplitude of was 5 mV. Finally, measuring the polarization curve. The scanning potential range was $-1.9$ V to $-1.1$ V, the scanning speed was $1$ mV s$^{-1}$.

The microstructure of alloys in varies states were observed and analyzed by optical microscope and scanning electron microscope (SEM), the surface morphology of immersion specimens that had been cleaned corrosion products was observed by SEM, the corrosion products were analyzed by x-ray diffraction.

3. Results and discussion

3.1. Microstructure

Figures 1 and 2 are the optical photographs and SEM images of Mg-4Nd-2Gd-0.5Zr alloys in different states. As shown in figures 1 and 2, the microstructure of the alloy is composed of $\alpha$-Mg matrix and the second phases distribute at the grain boundaries and grain interior. It can be observed from figure 2(a) that T4 alloy has fewer second phase that mainly distributed at grain boundaries, but the distribution is not uniform. The average grain size of T4 alloy is about $94 \pm 5$ $\mu$m measured by linear intercept method. At the initial stage of aging treatment, the grain size has not obvious change. The precipitated phase formed at the grain boundary firstly because the composition and energy fluctuation at the grain boundary are larger than those inside the grain, and the precipitated phase appeared in grain interior with the aging time extended. As can be seen from figures 2(b) and (c) that the precipitated phases on grain boundary gradually increase, and there are few granular phases is contained inside the grain. T6-8 h alloy shows uniform microstructure, the second phases at the grain boundaries is continuous or semi-continuous. As shown in figure 1, the grain size of alloys tends to increase with the further extension of aging time, the average grain size of T6-16 h alloy grew to $117 \pm 5$ $\mu$m. The amount of granular phases inside the grain increases gradually, and some precipitates become segregation, as shown in figures 2(d) and (e).

3.2. Corrosion performance

3.2.1. Weight loss rate

Table 1 shows the corrosion rate of alloys in different aging time after soaking in 3.5%NaCl aqueous solution for 1 day. As shown in table 1, the weight-loss corrosion rate of all alloys is much higher than the intrinsic corrosion.
rate of Mg, 0.3 mm y\(^{-1}\) [33], which shows that although the addition of rare earth elements improves the mechanical properties of magnesium alloy, the second phase in Mg-RE alloy has a positive electrode potential than the matrix, and the second phase forms a micro-battery with the matrix, which accelerates the corrosion of magnesium alloy. Therefore, it is of great significance to study the influence of aging treatment on the corrosion behavior of magnesium alloy. The corrosion rate of T4 alloy has the highest corrosion rate, 6.5 mm y\(^{-1}\). The corrosion rate decreases obviously after aging treatment, which shows that aging treatment can improve the corrosion resistance of the Mg-4Nd-2Gd-0.5Zr alloy. Among the tested specimens, T6-8 h specimen has the lowest corrosion rate, 3.6 mm y\(^{-1}\), and the value decreases by 45% compared with T4 specimen. But the corrosion rate increases significantly when the aging time of specimen is over 8 h, especially the corrosion rate of T6-12 h specimen is close to that of solid solution. Aging treatment can form precipitated phases in Mg-RE alloy, the matrix around the precipitated phase is preferentially corroded because it has a more negative potential, so the precipitated phase increases the corrosion acceleration. However, the second phases of magnesium alloy have a double effect on the corrosion of magnesium alloy. Mandal [34] and Song [35] et al had studied the corrosion behavior of AZ series magnesium alloys, the results revealed that grain refinement can improve the corrosion resistance, and the second phase can act as corrosion barrier as the second phase has a continuous distribution. Fu [36] and Zhang [37] also found this phenomenon that the continuous second phases can inhibit corrosion process in their studies on magnesium alloys. The second phases of T6-4 h specimen are less and the distribution is not uniform, the second phases of T6-8 h specimen are uniformly distributed along the grain boundaries. Therefore, the T6-8 h specimen has the lowest corrosion rate. When the aging time exceeds 8 h, the grain size of specimen and the number of granular phases increase, the precipitated phases segregate at grain boundary, which increase the number of galvanic corrosion, therefore T6-12 h specimen has higher corrosion rate than T6-8 h specimen. In T6-16 h specimen, the granular phase locates in grain interior form micro-battery.
with the surrounding matrix, which accelerates the corrosion of the matrix. The grain size of T6-16 h specimen is larger, which reduces the corrosion barrier of the grain boundary, and the second phase segregated at the grain boundary increases the cathode to anode area ratio, which also accelerates the corrosion [38, 39]. Therefore, the corrosion rate of T6-16 h specimen increase significantly. Over all, the results show that proper aging process can effectively improve the corrosion resistance of Mg-4Nd-2Gd-0.5Zr alloy.

### 3.2.2. Corrosion morphology and corrosion products

In order to further analysis the corrosion products of Mg-4Nd-2Gd-0.5Zr alloy after immersion in 3.5% NaCl solution, the corrosion products were identified by XRD, as shown in figure 3. The results show that the constituent of corrosion products is similar, primarily including Mg(OH)\(_2\) and a small quantity of Mg\(_{12}\)Nd and Mg\(_5\)Gd phases, it shows that some second phases falls off from matrix during corrosion process. Part of Mg(OH)\(_2\) will react with Cl\(^-\) to form soluble MgCl\(_2\) salt in solution containing Cl\(^-\), as shown in formula (3), hence the corrosion products collected in immersion test do not include MgCl\(_2\), and the XRD patterns of corrosion products not contain MgCl\(_2\) peak. The primary reactions in the corrosion process of magnesium alloy are the following formulas [40].

\[
\text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2\uparrow \\
\text{Mg(OH)}_2 + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + 2\text{OH}^- \tag{3}
\]

Figure 3 shows the corrosion morphology of Mg-4Nd-2Gd-0.5Zr alloys after immersion in 3.5% NaCl solution. Figures 4(a), (c), (e), (g), (i) is the SEM image of corrosion morphology, the black area is the uncorroded area, the corroded areas are river patterns. Figures 4(b), (d), (f), (h), (j) is the SEM image in backscattered electron mode, and the white particles are the second phase particles. It can be seen that the corrosion of the alloys is mainly local corrosion. After the specimens were immersed into NaCl solution, the surface of specimen was corroded first in local areas under the action of Cl\(^-\) erosion, resulting in corrosion pits. The corroded areas are prone to extend from corrosion pits to uncorroded areas along grain boundaries or impurities, river-like corrosion channel is formed with enlargement and deepening of the corrosion pits. There are corrosion particles fall off from the matrix, and expose the second phase particles. Local corrosion develops into uniform corrosion when the corrosion zones extend to the entire material surface. T6-16 h specimen suffered severe corrosion as shown in figures 4(i), (j), the corrosion morphology of T6-16 h specimen is almost uniform corrosion. It appears multiple corrosion forms in corroded surface of T6-16 h specimen, there have much of corrosion pits and intergranular corrosion. In T6-16 h specimen, there are lots of second phases segregated at grain boundary, the more nonuniform the distribution of second phases, the higher the activity of micro-battery formed between \(\alpha\)-Mg matrix and second phase, thus the substrate around the grain boundary is severely corroded, resulting in large corrosion pits. The corrosion pits expand from the grain boundary, resulting in intergranular corrosion morphology, as shown in figure 4(j). T6-16 h specimen also has lots of granular phases inside the grain, the matrix around these granular phases is corroded, resulting in corrosion pits. These corrosion characteristics prove that T6-16 h alloy has worse corrosion resistance.

Figure 3. X-ray diffraction patterns of corrosion products of Mg-4Nd-2Gd-0.5Zr alloys.
Figure 4. The SEM images of corrosion morphology (a) T4; (c) T6-4 h; (e) T6-8 h; (g) T6-12 h; (i) T6-16 h. The SEM (backscattered electron mode) images (b) T4; (d) T6-4 h; (f) T6-8 h; (h) T6-12 h; (j) T6-16 h.
3.3. Electrochemical test

3.3.1. Polarization curves

The potentiodynamic polarization curves of Mg-4Nd-2Gd-0.5Zr alloy under various aging times are shown in Figure 6. The potentiodynamic polarization curve has two branches, of which the cathodic branch represents the hydrogen evolution reaction. There are obvious differences in the slope of cathodic branches in different states, this shows that heat treatment has little effect on the cathodic hydrogen evolution. It is worth noting that the slope of anodic branch is larger than that of cathodic branch, this is because magnesium alloys have the negative difference effect (NDE) \( [41] \) in electrochemical corrosion process, the effect increases the rate of hydrogen evolution during anodic polarization. As shown in Figure 5, the polarization curves of the alloys in different states show similar shapes, both of all are asymmetrical, which indicates that the tested specimens show similar polarization behavior.

The corrosion current density and corrosion potential of the polarization curves were measured by Tafel extrapolation method \( [42, 43] \), as shown in Table 2. T4 specimen has the highest corrosion current density. Aging treatment decreases the corrosion current density, T6-8 h specimen has the lowest corrosion current density, and the value decreases by 74% compared with T4 specimen. While T6-12 h alloy and T6-16 h alloy have higher corrosion current density than T6-8 h alloy. In the study of Gao \( [42] \) and Atrens \( [32] \), the relationship between corrosion rate and corrosion current density is:

\[
P_i = 22.85i_{corr}
\]  

Where \( P_i \) is the corrosion rate from polarization curves, mm·y\(^{-1}\), \( i_{corr} \) is the corrosion current density. The results are listed in Table 2. Table 2 shows that the change rule of \( P_i \) is consistent with weight loss rate \( P_{wt} \). \( P_i \) decreases first and then increases, T8-8 h alloy has the lowest corrosion rate. But the value of \( P_i \) is much lower than weight loss rate. This is consistent with the results got by Atrens \( [33] \) and Bahmani \( [44] \).

3.3.2. Electrochemical impedance spectroscopy

The polarization behavior of magnesium alloy is not strictly comply with Tafel formula because of the negative difference effect. Therefore, EIS measurement was carried out to describe the effect of aging treatment on the corrosion behavior of Mg-4Nd-2Gd-0.5Zr alloy. Figure 6 shows the electrochemical impedance spectroscopy of

![Figure 5](image-url)

**Figure 5.** The polarization curves of Mg-4Nd-2Gd-0.5Zr alloy in various states.

**Table 2.** Corrosion parameters calculated from the polarization curves.

| State   | \( E_{corr} \) (V) | \( i_{corr} \) (10\(^{-2}\)mA·cm\(^{-2}\)) | \( P_i \) (mm·y\(^{-1}\)) | \( P_{wt} \) (mm·y\(^{-1}\)) |
|---------|-------------------|-----------------------------|-----------------|-------------------|
| T4      | −1.449            | 15.29                       | 3.49            | 6.6               |
| T6-4 h  | −1.513            | 4.414                       | 1.01            | 3.8               |
| T6-8 h  | −1.474            | 3.881                       | 0.89            | 3.6               |
| T6-12 h | −1.427            | 4.219                       | 0.96            | 4                 |
| T6-16 h | −1.457            | 5.573                       | 1.27            | 6.4               |
Mg-4Nd-2Gd-0.5Zr alloys in 3.5% NaCl solution. It can be found that the EIS curves of five alloys are similar in shape, which shows that aging treatment has no effect on the electrochemical process type of alloys in NaCl solution, but only changes the intensity of electrochemical reaction. In figure 6(a), the Nyquist plots of five alloys are comprise of three arcs (high frequency capacitance circuit, intermediate frequency capacitance circuit and low frequency induction circuit). The main difference of EIS plots of the five alloys is the variation of arc radius of intermediate frequency capacitance circuit. The arc radii of high frequency capacitance circuit and low frequency induction circuit are relatively small, showing that aging treatment mainly affects the change of intermediate frequency capacitance circuit. The small capacitance circuit in high frequency ranges is related to the adsorption on the electrode surface [45], which has little effect on the corrosion resistance of the specimen. The intermediate frequency capacitance circuit is caused by the charge transfer between the specimen surface and the corrosion medium. The larger the radius, the larger resistance of the corrosion film. T6-8 h specimen has the highest radius, which shows the surface film of T6-8 h alloy has the highest corrosion resistance compare with other state alloys. The low frequency induction circuit is related to the relaxation of corrosion products, which also means the formation of pit corrosion [26]. In Bode plots of $|Z|$-frequency curves shown in figure 6(b), T6-8 h specimen has the highest $|Z|$ value, T4 specimen has the lowest $|Z|$ value. In Bode plots of phase angle-frequency shown in figure 6(c), T6-8 h specimen have higher phase angle peak. Therefore, according to the EIS figures, the corrosion resistance of T6-8 h specimen is the best, while that of T4 specimen is the worst, which is consistent with the result of weight loss tests.

As mentioned above, the electrochemical characteristic of five alloys is same, hence it can be explained by the same equivalent circuit model. Based on the Nyquist and Bode plots, the equivalent circuit is shown in figure 7, the Nyquist fitting curves are shown in figure 7(a). In this equivalent circuit model, where $R_s$ is the solution resistance, $R_{ct}$ and CPE$_{dl}$ describe the charge transfer resistance and the capacitance of double electric layers respectively, $R_f$ and CPE$_f$ describe the resistance and the capacitance of surface film respectively, $R_l$ and L represent inductance and inductive impedance respectively. Table 3 shows the estimated values of electrochemical components obtained by Zview software. Polarization resistance $R_p$ is an important parameter to describe corrosion resistance, the larger $R_p$, the greater corrosion resistance. In this equivalent circuit model, $R_p$ can be calculated according to the following formula:

![Figure 6. The Nyquist (a) and Bode (b), (c) plots of Mg-4Nd-2Gd-0.5Zr alloys.](image-url)
As shown in table 3, the \( R_s \) values of five alloys are small, which indicates that the solution resistance has little effect on the electrochemical process. It can be seen that \( R_p \) values increase first and then decrease with aging time prolonging, which indicates that proper aging treatment can improve the corrosion resistance of Mg-4Nd-2Gd-0.5Zr alloy, which is consistent with the result of weight loss tests. The polarization resistance of T6-8 h specimen has the highest value, it proves that aging for 8 h can improve the corrosion resistance of the alloy to the greatest extent. In addition, according to the Stern formula \( \text{(46)} \), polarization resistance is inversely proportional to corrosion current, this shows that the larger the \( R_p \) value, the smaller the corrosion current density, and the corresponding corrosion rate is about lower. As shown in table 3, the value of \( R_p \) increases first and then decreases with the extension of aging time. According to the change trend of \( R_p \) values, T4 alloy has the lowest \( R_p \) value, hence T4 alloy has the highest corrosion rate in EIS experiment. The polarization resistance of T6-8 h alloy is highest, which shows that T6-8 h alloy has the lowest corrosion rate. When the aging time is prolonged, more precipitated phases increase the micro-galvanic corrosion, which increases the corrosion rate, hence the \( R_p \) value of the alloy becomes lower.

### 3.4. Corrosion mechanism

Magnesium is easy to form an oxide film on the surface of magnesium alloy in air because of its active chemical characteristics. This oxide film is mainly composed of MgO, the Pilling-Bedworth ratio of MgO/Mg is about 0.8 \( \text{[47, 48]} \), this oxide film has weak protective effect on matrix. MgO easily reacts with \( \text{H}_2\text{O} \) to form \( \text{Mg(OH)}_2 \) in 3.5% NaCl aqueous solution \( \text{[40]} \), as shown in formula (6), \( \text{Mg(OH)}_2 \) accumulates on the surface of the specimen to form a corrosion products film. But Mg(OH)_2 reacts with Cl\(^-\) to form soluble MgCl_2, as shown in formula (7). As the reaction proceeds, the corrosion products film is consumed and Mg(OH)_2 is shed, resulting in the alloy matrix is exposed to NaCl solution and is corroded.

\[
\text{MgO} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 \quad \text{(6)}
\]

\[
\text{Mg(OH)}_2 + 2\text{Cl}^- \rightarrow \text{MgCl}_2 + 2\text{OH}^- \quad \text{(7)}
\]

Micro-galvanic corrosion is usually formed when magnesium alloys are soaked in NaCl solution, the total chemical reaction is as shown in formula (8) \( \text{[40, 49]} \). The driving force of micro-galvanic corrosion comes from the potential difference between anode and cathode. The \( \alpha \)-Mg matrix has a negative potential than the surrounding second phases, therefore \( \alpha \)-Mg matrix acts anode to be oxidized to Mg\(^{2+}\) \( \text{[38]} \), as shown in formula (9). Reduction reaction occurs at the cathode, as shown in formula (10). Mg\(^+\) is a short-life intermediate \( \text{[50]} \) and eventually forms Mg\(^{2+}\) in aqueous solution, as shown in formula (11). Corrosion product Mg(OH)_2 is formed according to formula (12). Mg(OH)_2 gradually accumulates on the surface of the specimen to form a corrosion products film. This corrosion products film can isolate the specimen from corrosive medium and play a certain protective role. When Cl\(^-\) is present, the corrosion products film on the surface of the alloy will dissolve and even fall off.

\[
R_p = R_s + R_{ct} + (R_f + R_l) / (R_f + R_l) 
\] (5)
Total reaction: \( \text{Mg} + 2\text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{H}_2\uparrow \) \hfill (8)

Anodic reaction: \( \text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \) \hfill (9)

Cathodic reaction: \( 2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^- \) \hfill (10)

Chemical reaction: \( 2\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Mg}^{2+} + 2\text{OH}^- + \text{H}_2 \) \hfill (11)

Corrosion products: \( \text{Mg}^{2+} + 2\text{OH}^- \rightarrow \text{Mg(OH)}_2 \) \hfill (12)

As shown in figure 5, pitting occurred on the specimen surface. Figure 8 shows the schematic diagrams of corrosion mechanism. The first step of the pitting process is the adsorption of \( \text{Cl}^- \) on the surface. This adsorption does not take place uniformly, but at some points that may be the defects or impurities of the film. The adsorption of \( \text{Cl}^- \) makes the dissolution rate of the adsorbed region is faster than that of the film without \( \text{Cl}^- \) adsorption, and forms corrosion pits. After the formation of corrosion pits, \( \text{Cl}^- \) ions gather at the bottom of corrosion pits, which accelerates the dissolution of the matrix. The leakage of \( \text{H}_2 \) generated by cathode reaction will aggravate the destruction of the surface film, the existence of inductive reactance in the impedance spectrum also proves that the surface film break during corrosion process \([26, 51]\). The oxide film on the surface of the alloy is porous and uneven, there are some surfaces without oxide film coverage, and where the alloy matrix directly contacts with corrosion solution and is corroded \([41]\). The grain boundary that has segregation of the second phases and impurities has higher energy than matrix, which makes grain boundary is the sensitive area of corrosion. Pitting extends along the grain boundaries, lots of corrosion pits merge to form corrosion channels as shown in figure 4. With the corrosion process, the corrosion pits deepen, even produce the shedding of matrix. T6-16 h alloy has amounts of second phases that accumulate at the grain boundary, which accelerates corrosion of the matrix near the grain boundary. When corrosion pits develop to depth, the intergranular corrosion as shown in figure 4(e). The corrosion products of Mg-4Nd-2Gd-0.5Zr alloy in NaCl solution are mainly Mg(OH)$_2$. The corrosion products adsorb the alloy surface and gradually accumulate to form the corrosion products film, which plays a role in preventing corrosion. However, part of the corrosion products film will dissolve under corrosion action of \( \text{Cl}^- \), making the corrosion products film lose its adsorption and fall off from the specimen surface, resulting in the matrix is re-exposed to the corrosion medium and corroded.

As mentioned above, magnesium has low electrode potential \([14]\), and the second phase in Mg-RE alloy has a positive potential than the matrix, so the second phase forms micro-battery with the matrix, which accelerates the corrosion dissolution of the Mg substrate. Therefore, the second phase accelerates the corrosion dissolution of Mg in corrosion process. After the matrix is corroded and dissolved, the second phase falls off from the matrix because of the loss of adherence. In the study of Song \([35]\) and Fu \([36]\), the fine and continuous second phases is
not easily fall off by undermining, and the network second phases can prevent Cl\textsuperscript{−} form penetrating into the Mg matrix, which can retard the corrosion acceleration. Therefore, the second phase can also act as the corrosion barrier to prevent corrosion. In the experiment of this paper, aging treatment increases the quantity of the second phase on grain boundaries, and the distribution is more continuous, which can slow down the corrosion acceleration caused by the second phases and reduce the corrosion rate. The precipitation in T6-4 h alloy is less and unevenly distributed, while the distribution of the second phase in T6-8 h alloy is more uniform. The even distribution reduces the activity of micro-battery formed between Mg matrix and the second phase, which can less the corrosion acceleration. Hence, T6-8 h alloy has lower corrosion rate than T6-4 h alloy. With the extension of aging time, the quantity of precipitated phase gradually increase, while the second phases on the grain boundary is still maintaining its continuity, but its size is larger, the large size of the second phase increase the cathode to anode area ratio in galvanic corrosion, which accelerate the corrosion dissolution of matrix. In addition, the granular phase in grain interior also increase the corrosion rate. Therefore, the T6-12 h and T6-16 alloy have higher corrosion rate. In conclusion, the T6-8 h alloy has the lowest corrosion rate in the research range, which means that T6-8 h alloy has the best corrosion resistance.

4. Conclusion

(1) After heat treatment, the microstructure of Mg-4Nd-2Gd-0.5Zr alloy is consist of \(\alpha\)-Mg matrix and the second phases. The second phases are produced in the grain boundaries and grain interior after aging treatment. The second phases of T6-8 h alloy are uniformly and continuously distributed at the grain boundaries. When aging time is prolonged, the precipitates become segregate on grain boundaries and appear in grain interior, grain size tends to grow up.

(2) T4 alloy has the highest corrosion rate, while T6-8 h alloy has the lowest corrosion rate. The aging treatment can improve the corrosion resistance of Mg-4Nd-2Gd-0.5Zr alloy. According to the level of corrosion rate, the corrosion resistance of different state alloys is arranged as follows: T6-8 h > T6-12 h > T6-4 h > T6-16 h > T4.

(3) The grain size and the distribution and morphology of second phases act an important role on corrosion resistance of Mg-4Nd-2Gd-0.5Zr alloy. Small grains and continuous second phases can less the corrosion acceleration and thus improve the corrosion resistance, while large grains and coarsened second phases will accelerate the corrosion rate, and deteriorate the corrosion resistance.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Author contribution

Jianxin Liu: investigation, writing - original draft. Jun Chen: writing - review & editing. Quanan Li: writing—review & editing. Xiaoya Chen: writing—review & editing. Ziyan Zhang: investigation.

Conflicts of interest

The authors declare no conflict interest.

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