Effect of Nd on the microstructure and corrosion behavior of Mg-Gd-Nd-Zr alloys

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Keywords: Mg-Gd-Nd-Zr alloy, microstructure, corrosion behavior, corrosion mechanism, electrochemical test

Abstract

The corrosion behavior of Mg-12.5Gd-xNd-0.3Zr (x = 1, 2, 3 wt%) alloys were investigated by weight loss tests and electrochemical measurements in 3.5% NaCl solution. The results show that the increase of Nd content refine the grains gradually and promote the precipitates. Mg-12.5Gd-xNd-0.3Zr alloy is composed of α-Mg and MgGd and Nd₄₁Mg₅ phase, and the semi-continuous phase is formed with addition of 3% Nd. The corrosion resistance of Mg-12.5Gd-xNd-0.3Zr alloys sharply increases with the increase of Nd element by weight loss tests and the tendency is proven by means of electrochemical measurements. The corrosion resistance is improved when Nd content increases from 1% to 3% owning to the diminishing grain size and the change of distribution for second phase. The second phase play a dual effect on corrosion which depend on its distribution.

1. Introduction

Mg and its alloys have received a great attention in recent years because of expansion of demand for lightweight products and other domains due to their excellent creep properties, high strength, fine retrievability and other characteristics [2, 3]. However, Mg has high chemical reactivity and trend to be corroded especially in containing Cl⁻ solutions because its self-corrosion potential is only −2.37V at room temperature. Furthermore, the micro-galvanic corrosion is prone to occur between matrix and the second phase or impurities and it means the poor corrosion resistance even in the nature conditions [4].

The corrosion property of the alloys relies on their metallurgy and environmental factors. The metallurgical factors including grain size [5], second phase [6] and alloying elements [7] have important impact on corrosion behavior. The grain size has an ambivalent role on corrosion resistance because of chemical activity and diffusion rate [8]. In general, the grain boundary can improve the corrosion resistance depends on whether the existence passivation film. Choi et al [9] reported a fine-grained microstructure could improve densification which was contribute to reduce cracks in a protective film and corrosion layer. In addition, the second phase which is related to the micro-galvanic corrosion have the important influence on corrosion behavior which depend on distribution, morphology and potential of second phase [6, 10]. Song et al [11] found that the aged Mg-Zn alloy had the inferior corrosion property than solid-solution that owning to precipitates.

Numerous studies were conducted to improve the corrosion resistance by metallurgical manipulation and deformation process. Alloying is an effective measure to ameliorate unfavorable conditions and the addition of rare earth elements could significantly improve the corrosion resistance of magnesium alloys by means of purifying casting impurities, refining the grains and forming the stable protective films [12, 13]. Zhang et al [14] reported the corrosion potential of Mg-Zn-Y alloys decreased with Gd addition, and Mg-1Zn-1Y-0.5Gd showed the lowest corrosion rates which was related to the forming of uniform network-LPSO phase resulting in the lower self-corrosion current density. Chen et al [15] reported that the effect of Gd on corrosion properties of Mg-2Zn-0.5Zr alloy, and found that the corrosion resistance was improved with addition 0.5%–1% Gd the
uniformly distributed secondary phases which acted as barrier to prevent the corrosion while the galvanic corrosion happened resulting in reduced corrosion resistance between $\alpha$-Mg and increasing second phase when Gd content was up to 2%. Baek et al \cite{16} reported that addition of Y enhanced the corrosion resistance of extruded Mg-6Al-1Zn-0.5Ca-0.3Mn alloy due to the reduction of the electrochemical activity of Al-containing intermetallic compound. The Zr element is a common grain refiner for Mg-RE alloys and Zr could improve the corrosion resistance of Mg alloys. For instance, the corrosion resistance of Mg-6Al-3Zn alloy was increased with addition of Zr contributed to the forming of cathodic Al$_2$Zr phase protecting potentials of $\alpha$-Mg \cite{17}.

The Mg-Gd-Nd-Zr alloys have excellent mechanical properties and anti-creep properties \cite{18, 19}. Recently, Jiang et al \cite{20} investigated the corrosion behavior of Mg-3Y-xNd alloys, the Mg$_{14}$Y$_2$Nd phase and Mg$_3$(Y, Nd) phase played a dual effect on corrosion resistance. The Mg$_3$(Y, Nd) phase increased gradually while the Mg$_{14}$Y$_2$Nd phase got reserve as addition of Nd content, The Mg-3Y-1.5Nd alloy had the lowest corrosion resistance because Mg$_3$(Y, Nd) phase had the lower corrosion potential than that of Mg$_3$(Y, Nd) phase. Arrabal et al \cite{21} reported the impact of Nd on the corrosion behavior of AM50 and AZ91D, the results indicated that addition of Nd could suppress the diffusion of corrosion because Nd element reduced potential of cathode containing Nd phase and increased passivity of the surface. The Nd addition could refine the microstructure and form metal compounds. However, there are relatively few literatures connected to the corrosion behavior of Mg-Gd-Nd-Zr alloys containing high Gd elements. In order to understand corrosion properties of Mg-Gd-Nd comprehensively, it is very essential to investigate the Nd elements on corrosion behavior of Mg-Gd-Nd-Zr alloys.

In this work, the effect of Nd on the corrosion behavior of Mg-12.5Gd-xNd-0.3Zr alloys ($x = 1, 2, 3$) were investigated by weight loss test and electrochemical measurements. The variation of microstructure with Nd addition was analyzed. The effect of microstructure (grain size and second phase) on corrosion behavior was discussed with variable contents of Nd elements.

### 2. Experimental

#### 2.1. Materials preparation

The alloy ingots with nominal composition of Mg-12.5Gd-xNd-0.3Zr ($x = 1, 2, 3$) by melting high purity Mg (99.95 wt%), Mg-30 wt% Gd, Mg-30 wt% Nd and Mg-30 wt% Zr master alloys were prepared using a medium frequency induction furnace. In view of susceptible to oxidation during the preparation of Mg-30wt%Gd, Mg-30wt%Nd and Mg-30wt%Zr alloys, these master alloys were prepared under vacuum conditions ($3 \times 10^{-3}$ MPa). The ingots were heated to 750 °C for 5 min in furnace, In order to inflame retarding during smelting, pass a protective atmosphere of CO$_2$ and SF$_6$ mixed gas. and a metal mould with pre-heating to 250 °C was used to hold the alloy liquid. Then, the ingots were treated with solid-solution at 525 °C for 6h, and quenched into hot water about 60 °C. After solid-solution, the ingots were isothermally aged at 225°C for 12 h. The ingots of aged Mg-12.5Gd-1Nd-0.3Zr, Mg-12.5Gd-2Nd-0.3Zr and Mg-12.5Gd-3Nd-0.3Zr alloys are denoted as GN1, GN2 and GN3. The actual chemical composition of the alloys were determined by inductively coupled plasma (Optima 8000) which is shown in table 1. The specimens with dimensions of 10 mm × 10 mm × 10 mm were cut from the aged ingots for the microstructure observation, weight loss experiment and electrochemical tests.

#### 2.2. Microstructure characterization

The samples were grinded and polished with bright surface and then etched using 4% HNO$_3$ alcohol solution. The microstructure was detected by Axio Vert A1 optical microscope and JSM-2100LV scanning electron microscope equipped with energy dispersive spectrometer (EDS). The phases structures were detected by D8AX x-ray diffractometry (XRD).

### Table 1. Chemical composition of the Mg-12.5Gd-xNd-0.3Zr alloys (wt.%).

| Alloys | Chemical composition |
|--------|----------------------|
|        | Mg   | Gd  | Nd  | Zr  |
| GN1    | Bal. | 12.58 | 0.91 | 0.28 |
| GN2    | Bal. | 12.47 | 2.11 | 0.31 |
| GN3    | Bal. | 12.61 | 2.94 | 0.27 |
2.3. Weight loss test

The cubic specimens were immersed into 3.5% NaCl solution for 24h at room temperature. The weight of specimens was named \( M_1 \) before testing. After immersion tests, the corroded specimens were immersed into chromic acid solution \((200 \text{ g l}^{-1} \text{ CrO}_3 \text{ with } 10 \text{ g l}^{-1} \text{ AgNO}_3)\) to remove the corrosion products of the specimen surface. Then, the specimens were washed and dried. The final weight of specimens was named \( M_2 \). The corrosion rate \( P_w \) was calculated by the expression as following [22]:

\[
P_w = \frac{M_1 - M_2}{A \times t}
\]

**Figure 1.** XRD patterns of the Mg-12.5Gd-xNd-0.3Zr alloys. (a) GN1; (b) GN2; (c) GN3.

**Figure 2.** Optical microstructure of Mg-12.5Gd-xNd-0.3Zr alloys. (a) GN1; (b) GN2; (c) GN3.
\[ P_o = \frac{8.76 \times 10^4 \times \Delta w}{ATD} \]  

where \( \Delta W \) is the mass loss (g) which is \( M_1 - M_2 \); \( A \) is the surface area of the corroded alloys (cm\(^2\)); \( T \) is the immersion time (h); \( D \) is the density of the samples (g cm\(^{-3}\)).

2.4. Electrochemical measurements
The polarization curves and electrochemical impedance spectroscopy (EIS) of the specimens were measured in 3.5% NaCl solution using CHI660D electrochemical workstation at room temperature. The saturated calomel electrode (SCE) was used as a reference electrode, graphite as the auxiliary electrode, and the specimen with exposure area of 1 cm\(^2\) as the working electrode. Open-circuit potential was ensured to reached a stable value before EIS and polarization tests. The polarization curves began with \( -1.9 \) V/SCE and terminated at the \( -1.1 \) V/SCE, and the scanning rate was 1 mV s\(^{-1}\). The EIS were recorded in the sweep frequency range from 100 KHz to 0.1Hz with a sinusoidal signal perturbation of 5 mV. The EIS spectra were fitted by using the Zsimpwin software.

3. Results
3.1. The microstructure with Nd addition
Figure 1 shows the XRD pattern of Mg-12.5Gd-xNd-0.3Zr alloys. It can be seen that the \( \alpha \)-Mg and Mg\(_{5}\)Gd phase diffraction peak is found in the GN1 alloy. Strangely, the Mg\(_{41}\)Nd\(_{5}\) phase is not detected in the XRD pattern of the GN1 alloy. Generally, the critical content of the second phase detected by XRD is approximately 1\% - 2\% \[23\]. Hence, it is difficult to identify the small phase Mg\(_{41}\)Nd\(_{5}\) volume fractions in alloys for XRD. As the increase of Nd elements, the diffraction peaks of the Mg\(_{41}\)Nd\(_{5}\) phase appear in GN2 and GN3 alloys.

Figure 2 shows the optical microstructure of Mg-12.5Gd-xNd-0.3Zr alloys. It can be clearly observed that the Mg-12.5Gd-xNd-0.3Zr alloys are consist of \( \alpha \)-Mg matrix, grain boundary and dark second phase. Obviously, the grain size distribution of GN1 alloy is uneven and gross, and the grain refinement is achieved with increase of Nd elements. The grain size decreases sharply when the Nd element increases from 1\% to 3\% and the average grain size of three alloys is approximately 158 \( \mu m \), 96 \( \mu m \), 46 \( \mu m \), respectively. Obviously, Nd addition can obviously refine the grain size. The morphology and distribution of second phase are apparently various with Nd addition which is shown in figure 2 and the composition of the phase is required to further analysis.

Figure 3. SEM microstructure of the Mg-12.5Gd-xNd-0.3Zr alloys; (a) GN1; (b) GN2; (c) GN3.
Figure 3 shows the SEM microstructure of Mg-12.5Gd-xNd-0.3Zr alloys. The morphology and distribution of the second phase clearly were observed in the four alloys from figure 3. A phenomenon with dispersed clustered particles occurs in GN1 alloy. As the Nd addition, contrast to GN1 alloy, the cluster extent of particles has become more serious in GN2 alloy. Interestingly, it is found that the new semi-continuous network phase distributes along grain boundary in the GN3 alloy besides some clustered phase. The area fractions of second phases in GN1, GN2, GN3 alloys are 2.82%, 3.01% and 6.60%, respectively. Hence, the second phases not only distribute along the grain boundaries but also disperse within the grains. It has a significant increase in second phase for GN3 alloy. The EDS analysis is performed on the regions of the different marks in figure 3, and the results are shown in table 2. The precipitated clustered phase A at the grain boundary is mainly intermetallic compound composed of Mg, Gd, Nd, and Zr elements. The bright clustered particle D is the enrichment zone of Zr, and it is well-known that Zr-enriched particles can be used as heterogeneous nucleating agents for grain refinement [24]. The distribution of Nd and Gd in cubic phase marked B and C are shown in figure 3, and these cubic phases might be the hydrides by solution treatment. Zheng et al [25] found that the cuboid shaped phases was not still dissolved into Mg-matrix after solution treatment and be confirmed as the GdH2 type compound in the Mg-Gd-Nd-Zr alloy. Huang et al [23] found that the cubic phase was REs hydrides in Mg-(Gd, Dy, Y) alloys, and the formation of RE hydrides was dominated by the alloy casting and heat treatment. Zhu et al [26] concluded the similar results in Mg-(La, Ce, Nd) alloys. In addition, the Nd and Gd elements are enriched in the semi-continuous network phase E. According to the results of EDS and XRD analysis, the new phase potentially contains Mg5Gd and Mg41Nd5 phase.

### 3.2. Corrosion behavior

Figure 4 shows the corrosion rate of Mg-12.5Gd-xNd-0.3Zr alloys after immersion in 3.5% NaCl solution for 24 h. The corrosion rate obtained from the weight loss tests is the effective way to evaluate the corrosion resistance. It can be seen that GN1 alloy exhibits the largest corrosion rate which is 170 mm·y⁻¹ and the corrosion rate gradually decrease with Nd from 1wt% to 3 wt%. The intrinsic corrosion rate of high purity Mg of 0.3 mm·y⁻¹ as measured by weight loss of Mg in concentrated chloride solutions as the benchmark is lowest reliable corrosion rate in these solutions [12], and all the samples had a larger corrosion rate than high-purity Mg (0.3 mm·y⁻¹). It was reported that the diffusion coefficient of Nd is almost three times higher than those of Gd, which means that

![Figure 4. Corrosion rate of Mg-12.5Gd-xNd-0.3Zr alloys in 3.5% NaCl solution for 24 h.](image)

| Region | Mg wt.% | Gd at.% | Nd wt.% | Gd at.% | Zr wt.% | Zr at.% |
|--------|---------|---------|---------|---------|---------|---------|
| A      | 65.87   | 92.42   | 28.40   | 6.16    | 5.22    | 0.51    |
| B      | 67.56   | 92.95   | 27.16   | 5.78    | 4.91    | 0.37    |
| C      | 64.79   | 91.40   | 23.76   | 5.18    | 6.42    | 1.53    |
| D      | 12.79   | 36.63   | 8.11    | 3.59    | 2.02    | 77.07   |
| E      | 66.95   | 92.54   | 22.89   | 4.89    | 8.67    | 2.02    | 1.05    | 0.55    |

Figure 3 shows the SEM microstructure of Mg-12.5Gd-xNd-0.3Zr alloys. The morphology and distribution of the second phase clearly were observed in the four alloys from figure 3. A phenomenon with dispersed clustered particles occurs in GN1 alloy. As the Nd addition, contrast to GN1 alloy, the cluster extent of particles has become more serious in GN2 alloy. Interestingly, it is found that the new semi-continuous network phase distributes along grain boundary in the GN3 alloy besides some clustered phase. The area fractions of second phases in GN1, GN2, GN3 alloys are 2.82%, 3.01% and 6.60%, respectively. Hence, the second phases not only distribute along the grain boundaries but also disperse within the grains. It has a significant increase in second phase for GN3 alloy. The EDS analysis is performed on the regions of the different marks in figure 3, and the results are shown in table 2. The precipitated clustered phase A at the grain boundary is mainly intermetallic compound composed of Mg, Gd, Nd, and Zr elements. The bright clustered particle D is the enrichment zone of Zr, and it is well-known that Zr-enriched particles can be used as heterogeneous nucleating agents for grain refinement [24]. The distribution of Nd and Gd in cubic phase marked B and C are shown in figure 3, and these cubic phases might be the hydrides by solution treatment. Zheng et al [25] found that the cuboid shaped phases was not still dissolved into Mg-matrix after solution treatment and be confirmed as the GdH2 type compound in the Mg-Gd-Nd-Zr alloy. Huang et al [23] found that the cubic phase was REs hydrides in Mg-(Gd, Dy, Y) alloys, and the formation of RE hydrides was dominated by the alloy casting and heat treatment. Zhu et al [26] concluded the similar results in Mg-(La, Ce, Nd) alloys. In addition, the Nd and Gd elements are enriched in the semi-continuous network phase E. According to the results of EDS and XRD analysis, the new phase potentially contains Mg5Gd and Mg41Nd5 phase.
Nd elements has the more active behavior in Mg matrix [27]. The difference of two measurements is mainly caused by the factor that large number of precipitates would accelerate the degradation of \(\alpha\)-Mg matrix due to couple action. This indicates that the addition of Nd does improve the corrosion resistance of the Mg-Gd-Nd-Zr alloys by changing the microstructure.

Figure 5 shows the corroded surface photographs of Mg-12.5Gd-xNd-0.3Zr alloys after immersion in 3.5% NaCl solution for 24 h and removal of corrosion products; (a) GN1, (b) GN2, (c) GN3.

Figure 6 shows the SEM morphologies of Mg-12.5Gd-xNd-0.3Zr alloys after immersion in 3.5% NaCl solution for 24 h and removal of corrosion products; (a) GN1; (b) GN2; (c) GN3.
relatively uniform, but there are more honeycomb corrosion pits which are caused by galvanic corrosion. The characteristics on the corrosion surface may be resulted from the different order in the appearance of corrosion product protective film.

3.3. Electrochemical behavior

3.3.1. Polarization curves

Figure 7 shows the potentiodynamic polarization curves of Mg-12.5Gd-xNd-0.3Zr alloys in 3.5% NaCl solution. The instantaneous corrosion rate, \( P_i (\text{mm·y}^{-1}) \), was determined from the corrosion current density, \( I_{\text{CORR}} (\text{mA·cm}^{-2}) \), the formula is expressed as [16]:

\[
P_i = 22.85 \times I_{\text{CORR}}
\]

The fitting data of the polarization curves are listed in table 3. It can be seen that three tested alloys have the similar polarization curve shapes, implying that they have the similar electrochemical behaviors. Apparently, the increase of Nd does not lead a decrease in cathodic reaction kinetics for the test alloys. As the addition of Nd, the corrosion potential has no obvious shift. The corrosion potential \( E_{\text{CORR}} \) values of the alloys are \(-1.54\), \(-1.56\), and \(-1.48\) vs. SCE, respectively. Interestingly, the corrosion current density \( I_{\text{CORR}} \) of the alloys are not corresponding with variation tendency of \( E_{\text{CORR}} \) and its value is \(4.26 \times 10^{-1}\), \(2.66 \times 10^{-1}\), and \(1.54 \times 10^{-1}\) mA·cm\(^{-2}\), respectively. In fact, the \( E_{\text{CORR}} \) represents the thermodynamic parameter and its values just mirror the tendency of corrosion, while the \( I_{\text{CORR}} \) is the real kinetic parameter of corrosion reaction and its value reflects the corrosion rate [22, 28]. Obviously, the corrosion current density of GN1 alloy is highest implying that results of corrosion rate for GN1 alloy is corresponding with weight loss test. one can notice that electrochemical measurements provide the less corrosion rate value compared to corrosion rate \( P_w (\text{mm·y}^{-1}) \) measured by weight loss. The disagreement between weight loss and electrochemical measurements may be explained by the following reasons. One is that decoupling of the corrosion and electrochemical measurements may occur due to the evolving hydrogen and corrosion products. The other is that tafel extrapolation has typically been carried out to measure initial corrosion behavior after specimen immersion in the solution while the initial corrosion behavior may not correlate with steady corrosion behavior [12].

| Alloys | \( E_{\text{CORR}} \text{V/SCE} \) | \( I_{\text{CORR}} \text{(mA·cm}^{-2}) \) | \( P_i \text{(mm·y}^{-1}) \) |
|--------|----------------|----------------|----------------|
| GN1    | -1.54          | 4.26 \times 10^{-1} | 9.73            |
| GN2    | -1.56          | 2.66 \times 10^{-1} | 6.07            |
| GN3    | -1.48          | 1.54 \times 10^{-1} | 3.52            |

Figure 7. Polarization curves of Mg-12.5Gd-xNd-0.3Zr alloys in 3.5% NaCl solution.
3.3.2. Electrochemical impedance spectroscopy (EIS)

Figure 8 shows the Nyquist plots of Mg-12.5Gd-xNd-0.3Zr alloys immersed in 3.5% NaCl solution. As can be seen, these four alloys have the similar EIS spectra whereas the difference is the diameter of the loops with different alloy. The EIS spectra of three alloys all consist of a high-frequency capacitive loop, medium-frequency capacitive loop and a low-frequency capacitive loop implying that they probably have the same corrosion mechanisms. Referring to the relative literatures [28–31], the high-frequency loop appears to reflect charge transfer process between the working electrode and the solution medium. The medium-frequency loop is related to the relaxation process of mass transport for the reaction system owing to the growing corrosion products layer with increasing of immersion time [28, 29]. The low-frequency loop is attributed to the relaxation process of adsorbed products on the oxide layer [32]. In addition, the radius of capacitive reactance loop reflects the corrosion resistance of the alloys. The bigger radius value represents the higher corrosion resistance while the smaller radius value are inverse. Obviously, the radius of capacitive reactance loop for GN3 alloy, and GN1 has the smallest loop. Therefore, the ranking of corrosion resistance of the alloys can be written as: GN3 > GN2 > GN1. The results of EIS is in good agreement with the results of weight loss and polarization curves test from figures 4 and 7.

The equivalent circuit is fitted by means of the date of EIS spectra further to evaluate corrosion behavior of the alloys which is shown in figure 9. In this investigation, \( R_{s} \), \( R_{f} \) and \( R_{t} \) represent the solution resistance, charge transfer resistance and resistance of the oxide layer, respectively. The \( Q_{f} \) represents as the capacitor of the oxide layer, and \( R_{L} \) and \( L \) are the low-frequency pseudo resistance and inductance, respectively. It may be caused by
adsorption of corrosion products film. $R_{L\text{Mg}_2+}$ and $I_{\text{Mg}_2+}$ is the middle-frequency resistance and inductance. It is attributed to the reaction of Mg$^{2+}$ and H$_2$O at the deliquescent parts of corrosion products film [33, 34]. The fitting data of each circuit element from the equivalent circuit shown in figure 9 are listed in table 3. It can be seen from figure 8 that the fitting curves are basically corresponding with the original data indicating that the proposed equivalent circuit is reasonable and obviously reveals the overall corrosion process and mechanism of the alloy at various stages. According to the data shown in the table 3, $Q_{dl}$ could be regarded as the electric double layer capacitance of the anode because the values of constant phase element (CPE) is almost 1. The whole resistance fitted from equivalent circuit are normally used to evaluate corrosion properties of the alloys, and the relatively high value means the better corrosion resistance. The value of $R_{g}$, $R_{f}$ and $R$, determines the corrosion resistance. After fitting, it is found that GN3 alloy has the biggest resistance value while the GN1 alloy is lowest in four alloys. It indicated that GN3 have the best corrosion resistance while that are lowest in GN1 alloy.

4. Discussion

4.1. Effect of Nd addition on microstructure

It is evident that addition of Nd has a significant impact on grain sizes and precipitates from figures 2 and 3. As mentioned above, the grain size decreased sharply from 115 μm to 46 μm with addition of 3% Nd, implying that Nd is able to refine the microstructure dramatically which might be attributed to formation of Mg$_{41}$Nd$_5$ phase. The Mg$_{41}$Nd$_5$ phase could be the heterogeneous nucleation core of α-Mg during solidification. The edge-edge matching model [35, 36] acknowledges that it would be the effective sites of nucleation for the matrix in the solidification, when the intermetallic have a certain orientation relationship with the matrix. The orientation relationship must meet that mismatch degree on low exponential plane is less than 15% between the matrix and particles [36]. Chen et al [37] calculated the Mg$_{41}$Nd$_5$ and α-Mg coherent orientation of the number of relations. The mismatch results of (011)$_{\text{Mg}_{41}\text{Nd}_{5}}|(0001)_{\text{α-Mg}}$ (110)$_{\text{Mg}_{41}\text{Nd}_{5}}|(0001)_{\text{α-Mg}}$ (111)$_{\text{Mg}_{41}\text{Nd}_{5}}|(0001)_{\text{α-Mg}}$ are 1.52%, 5.23%, 6.74%, respectively. Therefore, Mg$_{41}$Nd$_5$ can act as the effective core of heterogeneous nucleation for α-Mg solidification, further resulting in refinement of the grain size. Su et al [38] and Zhang et al [39] also found the similar results by adding Nd element into Mg alloys. On the other hand, the refinement caused by Nd is related to the growth restriction of grains by solute elements segregation. Generally, the growth restriction factor (GRF) is employed to evaluate the solute effect. The value of GRF represents the extent of restriction of grain growth, and the higher value denotes the remarkable restriction effect [40]. According to the Mg-Gd and Mg-Nd binary phase diagram, the per-unit GRF values corresponding to Gd and Nd in Mg are 1.205 and 3.557, respectively [35]. And the value of GRF increases with Nd elements. It indicates that Nd element has the more remarkable restriction effect compared to Gd and results of refinements is more prominent with increasing of Nd addition. However, grain size distribution are uneven in GN1 alloy. A interesting phenomenon studied by Palival et al [27] was that diffusion coefficient of Nd is almost three times higher than those of Gd. It indicates that solute drag of Gd element exhibits more competitive on the grain boundary segregation in comparison with Nd element. In other words, the high diffusion of the solute Nd leads to the grain uneven. All in all, the a few addition Nd might result in uneven microstructure due to the powerful ability of diffusion, while the trend is not lasting with more Nd elements because of promoting the forming the heterogeneous nucleation core [41]. As can be seen from figure 3, the more precipitataion are observed with the addition of Nd. Apparently, precipitation is promoted by adding more RE elements. Moreover, the limited solid solubility of Gd decreases rapidly with the addition of Nd element. Hence, the result is expected generally. It is worth noting that the morphology of second phase vary dramatically with addition of Nd. The glomerate second phase is obvious in GN2 and GN3 alloy. The new phase in the form of semi-continuous network occurs distributing along grain boundary of GN3 alloy.

4.2. Effect of microstructure on corrosion behavior

Numerous studies were performed to reveal the relationship between grain size and corrosion behavior. Some researchers reported that refinement of grains dramatically decreased the corrosion resistance of Mg alloys. Luo et al [22] found that grain refinement reduced the corrosion resistance of as-extruded Mg-6Gd-2Y-xNd-0.2Zr ($x = 0, 0.5, 1, 1.5$) alloys due to the high density of grain boundaries promoting the formation of unstable oxide film. Song et al [42] also conducted that grain boundaries could not act as the corrosion barriers to delay corrosion due to having a high density of defects which is easier to lead to initiation of corrosion. However, it is reported that the alloys with the fine grain increased the corrosion resistance in previous work. Aung et al [43] investigated the effect of grain size on corrosion behavior of AZ31B alloy, and they suggested that the stronger chemical reactions occurs in the grain boundary, further promoting the formation of protective film. Liao et al [44] and suggested that grain boundary was the major crystallographic defects of polycrystal including magnesium alloys which acted as a corrosion barrier to impeded corrosion. In this work, the corrosion rate...
Table 4. EIS spectra fitting results of Mg-12.5Gd-xNd-0.3Zr alloys.

| Alloys | \( R_L \) (Ω) | \( R_f \) (Ω·cm\(^2\)) | \( Q_f \) (10\(^{-5}\) × μF·cm\(^{-2}\)) | \( n_1 \) | \( R_L \) (Ω·cm\(^2\)) | \( Q_{dl} \) (× µF·cm\(^{-2}\)) | \( n_2 \) | \( R_L \) (Ω·cm\(^2\)) | \( L \) (µH) | \( R_{LMG} \) (Ω·cm\(^2\)) | \( L_{MG} \) (µH) |
|--------|---------------|-----------------|-----------------|------|---------------|-----------------|------|---------------|------|-----------------|------|
| GN1    | 9.95          | 2.487           | 2.284           | 0.907| 25.11         | 3.488           | 1    | 214.2         | 6.60 | 91.9           | 11.07|
| GN2    | 9.46          | 9.238           | 3.589           | 0.840| 31.32         | 2.091           | 1    | 83.03         | 9.98 | 46.72          | 6.86 |
| GN3    | 10.34         | 6.511           | 2.543           | 0.893| 47.99         | 1.581           | 1    | 103.9         | 19.22| 83.22          | 43.34|

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gradually reduced with increasing of Nd from 1% to 3%, implying that the grain boundaries (GBs) has the important effect on corrosion behavior and the corrosion medium is 3.5 wt% NaCl solution with containing aggressive Cl\(^{-}\) ion environment. The grain boundaries (GBs) are able to act as a cathode to be not corroded and delays the spreading of corrosion due to the grain interior always have the more positive potential than that of the GBs [43]. Furthermore, the increase of the GBs density will reduce the concentration of impurities in the matrix and further decrease the negative effects of impurities on the corrosion resistance. As seen from figures 2(b)–(d), the GBs densities gradually increase with Nd addition and the corrosion resistance are the same as trend of the GBs densities. It must be pointed out that the grain size distribution of GN1 alloy is not extremely uniform and its influence on corrosion behavior is inevitable from figure 2(b). It is reported by Gollapudi et al [45] that a wider grain size distribution is more resistant to corrosion than a narrower that in the non-passivation environment. In terms of corrosivity, the uneven grain size is worse than uniform that when alloys is immersion in the environment with chloride ions which might be resulted from energy difference between uniform grains and uneven grain size. Considering this, it might be proved that the GN1 alloy has the worst corrosion performance in the alloys in GBs respects. Corrosion behavior may be explained in the alloys to a certain extent according to effect of grain size. Although GN1 has the lower GBs densities than that of two other alloys, in view of the role of second phase in three alloys, corrosion property of the alloys is worth to forward discuss.

With respect to alloying, chemical components have the dominant impact on corrosion resistance. In order to understand the corrosion behavior of alloys comprehensively, the effect of the second phase on that is worth to explore in addition to grain boundary. It is well-known that the second phase plays a dual role on corrosion behavior in Mg alloys. It can act as a cathode, further leading to accelerated galvanic corrosion between \(\alpha\)-Mg matrix and second phase. Interestingly, it can also act as a barrier further decreasing the corrosion transmitting in matrix due to the second phase has the lower chemical activity than the matrix. Zhao et al [46] proved that inconsistent roles second phase occurred in AZ91 alloy. They concluded that the second phase (\(\beta\)-phase) can accelerate micro-galvanic corrosion, while the \(\beta\)-phase in the form of a continuous network can act as a barrier and inhibit the corrosion propagation in AZ91 alloy. Song et al [47] also suggested the similar results. In the case of Mg-RE alloys, it is reported that the small size and uniform distribution of second phase can effectively improve the corrosion resistance due to the formation of the micro cell with low activity. As can be seen from figures 2 and 3, the second phase gradually increased with Nd addition, morphology and distribution of second phase are variant in three alloys. This indicates that second phase have an important role on corrosion behavior. Combined corrosion morphology and SEM from figures 3 and 6, the dispersive second phase accelerate the corrosion medium invading the matrix, and the most serious corrosion occurs in GN1 alloy because dispersed second phase would accelerate the galvanic corrosion in the environment with Cl\(^{-}\). Even though the maximum volume fraction of the second phase, the GN3 alloys eccentrically exhibits the better corrosion resistance compared to GN1 and GN2 alloy. As can be seen from figure 3(d), the new phase in GN3 alloy distributes near grain boundary in the form of semi-continuous network, implying that it might be formed the new corrosion barrier combined with grain boundary. However, a mass of voids are observed on the surface of GN3 alloy which means that the formations of the plentiful corrosion microcells is caused by many tiny particles and Mg matrix. The effect of Nd content on corrosion resistance of Mg-7Y-xNd alloys was reported [48], and the results showed that anti-corrosion property increased gradually with Nd addition because of change in the precipitations. The continuous distribution of \(\text{Mg}_{12}(Y, \text{Nd})\) inhibiting propagation of corrosion is increased and particle phase \(\text{Mg}_{24}(Y, \text{Nd})\) accelerating corrosion reaction is decreased with addition of Nd content. Thus, this phenomenon

![Figure 10. Schematic diagrams of corrosion mechanism for Mg-12.5Gd-xNd-0.3Zr alloys in 3.5%NaCl solution. (a) galvanic corrosion; (b) corrosion barrier.](image-url)
shows that morphology and distribution of the precipitations can reflect dual influence on the corrosion resistance of four alloys [46, 47]. The cluster phase and tiny precipitates have responsible for the worse corrosion performance in the alloys while the semi-continuous structure might serve as corrosion barrier. As a consequence, corrosion resistance is determined by second phase and grain size. For GN1 and GN2 alloy, the increased second phase lead to a enhance corrosion rate due to the micro-galvanic corrosion while the negative behaviors of second phase could be offset by the positive effect on corrosion resistance caused by grain refinement. For GN3 alloy, a large number of voids which is shown in figure 6(c) proved that the tiny second phase formed galvanic couple with matrix while the semi-continuous structure provided the effective corrosion barrier. The fitting dates of EIS measurement also provide the evidence to understand the corrosion behavior of Mg-Gd-Nd-Zr alloy. As can be seen from table 3, the film resistance of GN2 and GN3 alloy is more than that of GN1 which is attributed to the formation of the more corrosion production due to the increase of second phase.

In order to comprehend the corrosion mechanism of the alloys deeply, the schematic diagrams of corrosion for alloy-liquid interface which is shown in figure 9 is proposed based on the results in this work. The Mg-12.5Gd-xNd-0.3Zr alloys would be formed tight oxide film (MgO) in air. The oxide film with weaker anti-corrosion would dissolve immersed into the NaCl solution and the reaction expression is written as:

$$\text{MgO + H}_2\text{O} \rightarrow \text{Mg(OH)}_2$$  \hspace{1cm} (3)

Then, NaCl solution and Mg matrix which exposed to solution would have chemical reaction. The Mg is oxidized to Mg$^{2+}$, and hydrogen is formed on cathodic. In addition, Mg(OH)$_2$ corrosion product is formed on the corroded regions [49]. The expression is presented as follows.

$$\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^- \hspace{0.5cm} \text{(Anodic reaction)}$$  \hspace{1cm} (4)

$$\text{Mg}^{2+} + 2\text{H}_2\text{O} \rightarrow 2\text{Mg(OH)}_2 + \text{H}_2 \uparrow \hspace{0.5cm} \text{(Cathodic reaction)}$$  \hspace{1cm} (5)

It would be accompanied with the higher rate of reaction in interface, and the protective Mg(OH)$_2$ and H$_2$ would formed. The Mg(OH)$_2$ could be transformed into highly soluble MgCl$_2$ preferentially by Cl$^-$ ions [49]. The reaction equation is as follows.

$$\text{Mg(OH)}_2(s) + 2\text{Cl}^- (aq) = \text{MgCl}_2(aq) + 2\text{OH}^- (aq)$$  \hspace{1cm} (6)

It must be pointed that the galvanic corrosion is the dominated corrosion mechanism for the alloys and the involved chemical interactions include between α-Mg and second phase, and the second phase also have a reaction with solution. The results are that second phase might be oxidized, dissolved, dropped off and followed by the formation of corrosion pits. The abundant corrosion products accumulated and blocked the corrosion pits, which hindered the ion exchange the environment inside and outside and resulted in severe pitting corrosion. The corroded dispersive second phase would leave the more void which could offer the channel for Cl$^-$ ions to enter to the pits, and further expand the corrosion pits which is presented in figure 10(a). Nevertheless, when the Cl$^-$ ions close to grain boundary, it acts as corrosion barrier to prevent the propagation of corrosion. The grain boundary has the more anodic potentials compared to potential of α-Mg matrix to decrease reaction rate. In addition, as the Cl$^-$ ions permeation, the semi-continuous network phase has the significant function on preventing the propagation of corrosion as shown in figure 10(b). With the aggravation of pitting corrosion degree, the sectional matrix is preferentially dissolved with the sinking precipitates and it would accelerate the corrosion rate of the alloy.

5. Conclusion

(1) The Mg-12.5Gd-xNd-0.3Zr alloy is mainly composed of α-Mg and Mg$_5$Gd and Mg$_{41}$Nd$_5$ phase, and second phase increase with increasing of Nd content. The semi-continuous network phase is formed in Mg-12.5Gd-3Nd-0.3Zr alloy and the addition of Nd refines the grains of the alloys.

(2) The corrosion resistance of Mg-12.5Gd-xNd-0.3Zr alloys increases with Nd content increasing from 1% to 3%, and Mg-12.5Gd-3Nd-0.3Zr alloy has the highest corrosion resistance. The higher grain boundaries densities act vital corrosion barrier to prevent the propagation, and uneven grain size distribution will accelerate corrosion.

(3) The second phase plays a dual role on corrosion behavior, and semi-continuous network phase in Mg-12.5Gd-3Nd-0.3Zr alloy is able to act a corrosion barrier while the dispersed and cluster phase would cause deterioration of corrosion resistance.
Acknowledgments

This project is sponsored by the National Natural Science Foundation of China (Nos. 51571084).

Data availability statement

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

Declaration of competing interest

The authors declare no conflict interest.

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