Effect of Different Scale Precipitates on Corrosion Behavior of Mg–10Gd–3Y–0.4Zr Alloy

Shuang Yu^{1,3} · Rui-Ling Jia¹ · Tao Zhang² · Fu-Hui Wang² · Jian Hou³ · Hui-Xia Zhang³

Received: 2 May 2018 / Revised: 16 June 2018 / Published online: 14 September 2018
© The Chinese Society for Metals and Springer-Verlag GmbH Germany, part of Springer Nature 2018

Abstract

A large amount of directional and willow-like β' phase was precipitated in Mg–10Gd–3Y–0.4Zr (GW103K) alloy after solution treatment and subsequently aged treatment (T6). In order to explore the effect of the precipitates on the corrosion behavior of the GW103K alloy, the alloy was subjected to solution treatment (T4) at 773 K for 4 h at first, subsequently aged at 498 K for 193 h (T6). The microstructure evolution of the GW103K alloy after this treatment was investigated by scanning electron microscopy and transmission electron microscopy. The high-angle annular detector dark-field scanning transmission electron microscopy was used to observe the typical corrosion morphologies of the nanoscale precipitation phases (β') in the T6-treated alloy. The corrosion rate was measured by potentiodynamic polarization test. Combining with the potential measurement results by scanning Kelvin probe force microscopy, the effects of the skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ and β' precipitates on the corrosion behavior of GW103K alloy were explored. The results showed that the corrosion rate of the GW103K alloy in different conditions was ranked as: as-cast alloy > T4-treated alloy > T6-treated alloy, attributing to the fact that the relative potential differences of skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ were lower than those of the matrix, therefore $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase formed micro-galvanic coupling with the matrix and corrosion dissolution occurred. The nanoscale β' precipitates in T6-treated alloy can retard the cathodic process.

Keywords Magnesium alloy · Aging precipitates · Corrosion · Potential difference · Transmission electron microscopy (TEM)

1 Introduction

Magnesium alloy is the third type of metallic structural materials followed by steel and aluminum alloy [1]. It has the excellent mechanical performance such as high specific strength and stiffness, easy casting and processing, so it is widely used in aviation, aerospace, transportation, military, national defense engineering and other fields [2–4]. In

decade years, rare earth (RE) has been widely used as alloying elements because they can significantly optimize the mechanical properties of magnesium alloy, due to RE electronic structure outside the nucleus [5–8]. Mg–Gd system is one of the most promising application candidates. In particular, when Mg–Gd alloy is treated with aging treatment, the nanoscale precipitates and long-period stacking-ordered (LPSO) structure have excellent thermal stability, which is greatly helpful to improve its tensile strength at room temperature [9], yield strength [10], peak hardness, heat resistance [11], corrosion resistance [12], impact toughness and plane-strain fracture toughness [13].

Mg–Gd–Y–Zr alloy (adding a small amount of Zr will play a role in grain refinement [14]) exhibits a four-stage precipitation sequence during aging at 200–250 °C, i.e., α' -Mg (SSSS) $\rightarrow \beta''$ (DO_{19}) $\rightarrow \beta'$ (cbco) $\rightarrow \beta$ (fcc). This means that the supersaturated solid solution (SSSS) via the intermediate meta-stable precipitates β'' and β' finally transforms into the equilibrium precipitates β [15, 16]. Li et al. [17] have discovered that β'' is a meta-stable phase

Available online at <http://link.springer.com/journal/40195>

✉ Rui-Ling Jia
jiaruilong2018@163.com

¹ School of Materials Science and Engineering, Inner Mongolia University of Technology, Hohhot 010051, China

² School of Materials Science and Engineering, Northeast University, Shenyang 110819, China

³ State Key Laboratory for Marine Corrosion and Protection, Luoyang Ship Material Research Institute (LSMRI), Qingdao 266101, China

and its crystalline structure is DO₁₉ structure (hexagonal closest packing (hcp), lattice parameters $a_{\beta''} = 2a_{\alpha\text{-Mg}}$, $c_{\beta} = c_{\alpha\text{-Mg}}$) and that β' is mostly c -axis base-centered orthorhombic (cbco) structure, and face-centered cubic (fcc) structure (Mg–Nd) or rhombohedral structure (Mg–Pr) can also exist [18, 19].

At present, some studies showed that the Mg–Gd–Y–Zr alloy has achieved relatively good mechanical properties and corrosion resistance. But its corrosion mechanism is greatly different from that in traditional AZ series magnesium alloy. Song et al. [20] found that the Mg₂₄Y₅ phase in the as-cast GW93 alloy exhibited more negative potential and higher chemical activity. The Mg₂₄Y₅ phase acted as anode was preferentially corroded during the corrosion process of the GW93 alloy. Liu et al. [21] discovered that the dendritic-like phase rich in Y, Gd and Nd in the as-cast EW75 alloy acted as a micro-anode was also preferentially dissolved in the corrosion process. For GW103K alloy, the β' phase formed by RE and Mg can be precipitated from supersaturated α -Mg matrix after aging treatment. This makes the corrosion behavior of the aged GW103K alloy become more complex. Peng et al. [22] reported the corrosion behavior of Mg–10Gd–3Y–0.4Zr alloy after T4 and T6 treatments. Liang et al. [23] analyzed the corrosion mechanism by studying the corrosion products in Mg–7Gd–3Y–0.4Zr alloy under different treatment conditions. However, these research works paid more attention to the uniform corrosion of the alloys. The effect of precipitates of the Mg–Gd–Y alloy on its corrosion susceptibility was not investigated well. As mentioned above, there are different precipitates formed in Mg–Gd–Y–Zr alloy after heat treatment. The corrosion susceptibility of Mg–Gd–Y–Zr alloy depends considerably on the composition, amount and the relative potential difference of the precipitates presented in the alloy. The aim of the present work is to determine the effects of different precipitate phases on the corrosion behavior of Mg–10Gd–3Y–0.4Zr alloy under different heat treatment conditions.

2 Experimental

2.1 Heat Treatment

An as-cast Mg–10Gd–3Y–0.4Zr alloy was cut into a small cuboid with a size of 10 mm×10 mm×30 mm using wire cutting. The solid solution treatment (T4) was carried out at 773 K for 4 h in an electric resistance furnace under the shelter of CO₂ and SO₂ gases which generated from the decomposition of mixed CaCO₃ and FeS₂. The electric resistance furnace was preheated to 300 °C before the T4 heat treatment. The specimens were quenched into hot water at 80 ± 3 °C after the T4 heat treatment. The aged

treatment was followed the T4 treatment by precipitation tempering at 498 K for 193 h.

2.2 Microstructure Analysis

The specimens for microstructure observation were prepared by a conventional mechanical polishing technique. A field emission scanning electron microscope (FE-SEM, SIGMA 500) with energy-dispersive spectroscopy (EDS) and a transmission electron microscope (TEM, JEM-2100) were used to analyze the microstructure. The specimens for TEM measurements were ground to ~ 100 μm thick by 1000-grit silicon carbide papers, subsequently thinned by ion milling.

2.3 Corrosion Characterization

The potentiodynamic polarization measurement was tested using three-electrode systems by a Zahner electrochemical workstation (Zennium). A large-area platinum sheet was used as a counter electrode, with the saturated calomel electrode (SCE) as the reference electrode and specimens as the working electrode. (The exposed working area was approximately 1.0 cm².) The experiments were carried out in 3.5 wt% NaCl solution. The scanning potential range of the potentiodynamic polarization testing is – 2.5– (– 0.5) V, and the scanning speed is 1 mV/s. The experiments were carried out at room temperature. To ensure the stability of the open-circuit voltage, the measurement was taken after immersion in 3.5 wt% NaCl aqueous solution for 60 min.

The specimens for immersion testing were polished successively on 2000-grit abrasive paper. The specimens were immersed in 3.5 wt% NaCl aqueous solution for 10 min or 120 min at 25 ± 2 °C. After immersion testing, corrosion products on the surface were removed by immersing in a solution of 200 g/L CrO₃ and 10 g/L AgNO₃ at ambient temperature for 3 min. The corrosion morphologies of the specimens after removing corrosion products were observed by optical microscopy (OM; Axio Imager A1 M) and FE-SEM. Another immersion testing for observing corrosion morphologies of β' structure was performed in 1 mol/L NaCl aqueous solution for 15 min. The prepared T6-193 TEM specimens which experienced the immersion testing were cleaned in distilled water, dried and transferred into the HAADF-STEM for further investigation.

Volta potential distributions of the GW103K alloy were measured by a scanning probe microscopy (SPM, Multi-mode 8.0) equipped with a scanning Kelvin probe force microscopy (SKPFM) working in tapping mode. Surface potential maps were obtained using a silicon tip on nitride level (PFQNE-A1) under the peak force mode. The tested

specimens were polished to a 0.3 μm alumina polishing suspension. All measurements were taken in air at room temperature, and the relative humidity was in the range of 40–65%. The topography and the potential between probe and specimen were scanned with a pixel density of 512×512 and with a scan frequency of 0.5 Hz.

3 Results and Discussion

3.1 Characterization of Microstructure

Figure 1 presents the microstructures of the GW103K alloy under as-cast, T4 treatment and T6 treatment conditions. The images obtained by SEM show different contrast on the different phases; the dark regions represent the magnesium matrix ($\alpha\text{-Mg}$), whereas the lighter color represents intermetallic phases. Figure 1a shows the microstructure of the as-cast GW103K alloy, the skeleton-like phases distributed along the grain boundaries, and the size of this kind of phase is about 5–30 μm . A light-gray contrast area around the skeleton-like phases can be seen in Fig. 1a. Zhang et al. [24] believed it was a series of dendrite segregation along the grain boundary formed by Gd and Y elements in the as-cast Mg–9.42Gd–2.13Y–0.42Zr alloy, and this dendrite segregation can be eliminated during the solid solution treatment. EDS analysis is shown in Fig. 1b.

It suggests that the skeleton-like phases are composed mainly of three elements: Mg, Gd and Y. After T4 treatment, some refined skeleton-like phases and cuboid-shaped precipitates on the grain boundaries can be observed in Fig. 1c. After T6 treatment, the skeleton-like phases are precipitated again along the grain boundaries, but the amount of them decreases compared to that in the as-cast alloy.

We use TEM to determine the composition and crystal structure of dominated intermetallic phase formed in the as-cast GW103K alloy. Figure 2 displays the bright-field image and typical electron diffraction patterns of the skeleton-like phase. According to the diffraction pattern of the skeleton-like phase in Fig. 2b, the pattern can be indexed to the zone axis of the intermetallic phase with a body-centered cubic crystal structure [25, 26]. The calculated lattice parameter of the intermetallic phase is $a = 11.20 \text{ nm}$. The structure is the same as that of Mg_{24}Y_5 . As shown by the EDS analysis in Fig. 1b, it can be speculated that Gd element enters Mg_{24}Y_5 instead of part Y element to form $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ [27].

For the Mg–Gd–Y–Zr alloy, the structures of the precipitates and structural transformation processes over the aging time have been reported and the majority of the precipitates are β' phase under the 193-h over-aged condition [28]. Figure 3 exhibits the morphologies and selected area electron diffraction (SAED) patterns of the β'

Fig. 1 SEM images and EDS analysis of GW103K alloys: **a** as-cast; **b** EDS analysis of skeleton-like phase in **a**; **c** T4 treatment; **d** T6 treatment

Fig. 2 TEM analysis for as-cast GW103K alloy: **a** bright-field image of skeleton-like phase; **b** SAED pattern of skeleton-like phase

Fig. 3 β' phase in GW103K alloy after aging at 498 K for 193 h: **a** TEM image; **b** SAED pattern; **c** high-resolution TEM image taken along $\langle 0001 \rangle_{\text{Mg}}$ zone; **d** the corresponding FT patterns. The ring indicates the mask location used for inverse fast FT (FFT) and processed image after inverse FFT corresponding to **c**

phase. There are many willow-like precipitates uniformly dispersed within the T6-treated GW103K alloy in Fig. 3a. Zheng et al. [18] have reported that the willow-like β' phases have the cbco structure, the precursor of the β' phase nucleus has the DO_{19} structure, and the nucleation of the β' phase was formed by the ordering of RE atoms into several atomic layers to become a DO_{19} structure and then stacking periodically in the $\langle 1\bar{1}00 \rangle_{\text{Mg}}$ direction. Figure 3b

is a selected area electron diffraction pattern along $[0001]_{\alpha}$ axis. Since β' phase and α -Mg matrix are completely coherent, two sets of diffraction patterns are found in Fig. 3b, of which the brighter positive six corner patterns are the diffraction patterns of α -Mg matrix, and the five distinct patterns marked at the white square are diffraction patterns of β' phase. The orientation relationship between β' phase and α -Mg matrix is $(001)_{\beta'} // (0001)_{\alpha}$,

$[100]_{\beta'}/[10\bar{1}0]_{\alpha}$, and the lattice parameters of β' phase are $a = 2a_{\alpha\text{-Mg}} \approx 0.64$ nm, $b = 8d_{(10\bar{1}0)_{\alpha\text{-Mg}}} \approx 2.22$ nm, $c = c_{\alpha\text{-Mg}} \approx 0.52$ nm (d is the crystal plane spacing) [18, 29]. From the high-resolution TEM image shown in Fig. 3c, a strongly connected microstructure consisting of platelets is observed. The type of platelet structure depends on the aging time. Antion et al. [30] found that the platelet precipitates were of β'' phase after aging for less than 2 h, whereas β'' precipitates were turning into the β' phase after aging 2 h. Invert Fourier transform (FT) was carried out on these platelet precipitates' images (the inset in Fig. 3d), which indicates the precipitate is the periodic stacking of three layers. The Mg atom is sandwiched between the layers containing RE atoms. The result is consistent with the β' phase described in Ref. [31].

3.2 Corrosion Behavior of GW103K Alloy in Different Conditions

3.2.1 Potentiodynamic Polarization

Figure 4 presents the potentiodynamic polarization curves of GW103K alloys in different conditions after immersion in 3.5 wt% NaCl solution for 60 min. The slope of the cathodic branch is much steeper than that of the anodic branch, which indicates the cathodic reaction plays a major role in the whole corrosion process. Generally, the cathodic branch is deemed to represent the cathodic hydrogen evolution, and the anodic ones represent the dissolution of magnesium. It can be seen in Fig. 4 that the cathodic polarization current of hydrogen evolution reaction on as-cast GW103K sample is higher than other two alloys with T4 and T6 treatments [23]. Especially for the T6-treated alloy, the cathodic process is markedly retarded. Table 1 lists the corrosion potential (E_{corr}), corrosion current

density (I_{corr}), slope of anodic polarization (β_a), slope of cathodic polarization (β_c) and polarization resistance (R_p) values for the corresponding specimens. The corrosion rate can be evaluated from the corrosion current density (I_{corr}). The I_{corr} value of the as-cast GW103K alloy is the highest. After T4 treatment, the I_{corr} value is slightly decreased. For T6-treated alloy, the corrosion current density is significantly decreased and the polarization resistance (R_p) is the largest in all conditions. The decreasing order of corrosion rate of GW103K alloys in different conditions is as follows: as-cast condition > T4 condition > T6 condition.

3.2.2 Corrosion Morphologies

The differences in corrosion morphologies among GW103K alloys in three conditions are investigated by SEM. Figure 5 reveals the SEM images of corrosion morphologies of GW103K alloys in three conditions after immersion in 3.5 wt% NaCl solution for 10 min. It can be found that the serious corrosion attack has occurred along the grain boundaries of the as-cast GW103K alloy. It indicates that the chemical properties of the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase distributed along the grain boundaries are more active than those of the α -Mg matrix, and priority dissolving during the corrosion process. For the T4-treated alloy, several deep pits can be seen on the surface, the refined skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases are preferentially dissolved and cuboid-shaped precipitates have not corroded (circle-marked places in Fig. 5b). A lot of light corrosion pits are presented on the surface of T6-treated alloy shown in Fig. 5c (circle-marked places). At this period, the β' precipitates dissolve preferentially than the skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ during the corrosion. From the metallographic image of the T6-treated alloy after immersion in 3.5 wt% NaCl solution for 30 min (Fig. 5d), the size of tiny pits is evaluated about several hundred nanometers, and the corrosion behavior of the T6-treated alloy is probably related to the β' precipitates. Similar corrosion morphologies of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ can be seen in Fig. 5d (circle-marked places).

A series of nanometer-sized precipitates were the main strengthening sources for Mg–Gd–Y–Zr alloy after aging treatment. However, it is still not clear about the effects of these precipitates on the corrosion behavior of Mg–Gd–Y–Zr alloy because the electrochemical behavior of the nanometer-sized precipitates is too difficult to distinguish by measurement tools with low spatial resolution. TEM technique with high-angle annular detector dark-field (HAADF) mode can be employed to observe the corrosion morphologies of nanometer-sized phases [32]. Figure 6 reveals the morphologies of β' phases before and after immersion. Figure 6a is the HAADF image showing the morphologies of β' phases with willow leaves shape in the

Fig. 4 Potentiodynamic polarization curves of GW103K alloy in different conditions

Table 1 Electrochemical parameters obtained from potentiodynamic polarization curves

Material	E_{corr} (vs. SCE)	I_{corr} (A/cm ²)	β_a (V/dec)	β_c (V/dec)	R_p (Ω cm ²)
GW103K-F	− 1.389	1.78E−4	0.125	− 0.267	573.453
GW103K-T4	− 1.429	1.04E−4	0.116	− 0.253	894.756
GW103K-T6-193 h	− 1.449	7.21E−5	0.112	− 0.247	1145.033

Fig. 5 Corrosion morphologies of GW103K alloys in different conditions after immersion in 3.5 wt% NaCl solution for 10 min: **a** as-cast; **b** T4 treatment; **c** T6 treatment; **d** metallographic image of T6-treated alloy immersed in 3.5 wt% NaCl solution for 30 min **Fig. 6** **a** HAADF image showing morphologies of β' phases; **b** HAADF image showing corrosion morphologies of β' phases after immersion in 1 mol/L NaCl solution for 15 min; **c** SEM image showing corrosion morphology of alloy after immersion in 3.5 wt% NaCl solution for 2 h for GW103K alloy in T6 condition

T6-treated alloy. After immersion in 1.0 mol/L NaCl solution for 15 min, the corrosion morphologies of the β' phases in the T6-treated specimen are also observed using the STEM, as shown in Fig. 6b, and the selective dissolution of the β' phases is obvious. The electrochemical effect of the nanometer-sized β' phases is to directly affect the corrosion behavior of the T6-treated GW103 alloy. The small dissolution pits with strip shapes on the surface of the T6-treated GW103K alloy are shown in Fig. 6c, which should be ascribed to the dissolution of the β' precipitates.

3.3 Surface Potential Measurements by SKPFM

It is well known that the relative Volta potential differences between the precipitates and the matrix have a strong effect on the local corrosion of the alloys. Considering the work function mode of SKPFM, the darker color in the Volta potential map means more negative potential, while the lighter color means nobler potentials. Figure 7 shows topographic and three-dimensional potential maps using SKPFM. Figure 7a shows the morphology of the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase in the as-cast GW103K alloy. Figure 7b exhibits the 3D distribution of potential; the potential of the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase is similar to that of the α -Mg matrix, but the potential of the dendrite segregation area rich in Gd and Y elements around $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase is higher, which is characterized by a Volta potential difference by 140–190 mV between the dendrite segregation area rich in

Gd and Y elements and the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase. Figure 7d shows the morphology of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ in the T6-treated alloy, which is characterized by a difference in Volta potential with respect to the matrix about -160 mV. The results of SKPFM measurements show that the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases are anodic compared to the dendrite segregation area rich in Gd, Y or the matrix in both the as-cast and T6-treated GW103K alloys. From the SEM images shown in Fig. 1, it can be noticed that the volume fraction of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases in the alloy decreased obviously with 193-h aging treatment, so the corrosion behavior of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase is not the major affect factors during the corrosion of the T6-treated alloy.

Figure 8 exhibits the morphologies and the potential maps of β' phase in the GW103K alloy after 193-h aging treatment. Figure 8a is the HRTEM image of β' phases. The β' phase is directional and the size is about 50–100 nm, so the scanned area of SKPFM measurement is set at $100 \text{ nm} \times 100 \text{ nm}$. Figure 8b shows β' phase with light contrast in the white circle. Figure 8c is the potential map, and Fig. 8d is the line profile analysis corresponding to the line L3, which presents the potential of β' phase is lower than that of the matrix and the potential difference between them is about 20–50 mV after repeated measurements. There is no obvious potential difference between β' phases and the matrix, so it cannot be related to the β' phase occur preferential dissolution. Considering the interlayer structure of Mg and RE atoms of the β' phase in

Fig. 7 AFM surface topographies **a, d**; 3D potential maps **b, e**; and potential profile of skeleton-like phases **c, f** in as-cast GW103K alloy **a–c** and GW103K alloy after aging treatment **d–f**

Fig. 8 Morphologies and potential map of β' phase in t GW103K alloy after 193-h aging treatment: **a** HRTEM image; **b** AFM surface topography; **c** two-dimensional potential map; **d** line profile analysis corresponding to the line L3 shown in **c**

Fig. 3, the corrosion dissolution of the β' precipitates owing to the chemical properties of Mg atoms is more active than the RE atoms; the interlayer structure increases the contact area between the Mg atom and the RE atoms, making it more susceptible to perform electrochemical reaction. The corrosion behavior of the β' precipitates plays a key role during the corrosion of the T6-treated alloy.

4 Discussion

The corrosion mechanism of GW103K alloys in different conditions can be discussed in terms of the relative potential difference and corrosion phenomena. For the as-cast alloy, the microstructure consists of a lot of skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$, so the corrosion behavior of the alloy is mainly determined by the electrochemical effect and hydrogen evolution reaction of the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$. Combining corrosion morphologies (Fig. 5a) and the potential map (Fig. 7b), it can be inferred that the $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ acts as the anode to corrode preferentially. Thus, the corrosion morphology of the as-cast GW103K alloy is characterized by some obvious corrosion pits which are caused by the corrosion dissolution of skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase.

Song et al. [20] also found similar corrosion of Mg_{24}Y_5 phase in the as-cast GW93 alloy. Hydrogen evolution reaction of the precipitate also plays an important role during the corrosion process. A large number of continuous skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases exist in the as-cast GW103K alloy; therefore, the hydrogen evolution reaction of the as-cast alloy is very intense during the corrosion process, and the cathodic polarization current in the polarization curve is higher than that of both T4-treated and T6-treated alloys. From another point of view, according to the law of Faraday, corrosion current density is proportional to the corrosion speed and it also can be deduced that the value of corrosion current density tends to enlarge because of continuous skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases in the as-cast GW103K alloy (Fig. 4). Liang et al. [23] also found that the change in the microstructure of the GW73 K alloy under T4 and T6 treatments resulted in the obvious change in the cathodic branch of their polarization curves.

Most precipitates dissolved in the matrix of the GW103K alloy after T4 treatment, and only a small amount of refined skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases and cuboid-shaped precipitates was distributed along the grain boundaries (Fig. 1b), which occurred by the corrosion dissolution of refined skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases ,

and the cuboid-shaped precipitates have no obvious corrosion after immersion. Compared to the as-cast GW103K alloy, the skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases at the grain boundary decreased significantly and the hydrogen evolution reaction was weakened during the corrosion process of T4-treated alloy. Therefore, the polarization resistance increased and the corrosion current density decreased obviously of the polarization curve of the alloy after T4 treatment (Fig. 4).

After 193-h aging, skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ tends to segregate from the supersaturated matrix (Fig. 1c) and the nanoscale β' precipitates uniformly disperse within the matrix (Figs. 3a, 6a and 8a). From the observation of corrosion morphologies in Fig. 5c and d, it can be known that $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ is corroded during corrosion process. The potential differences between $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ and α -Mg matrix in the GW103K alloy after aging treatment are similar to that in the as-cast alloy. However, the interlayer structure of β' precipitates in the T6-treated alloy is more susceptible to occur preferential dissolution. The corrosion behavior of the T6-treated alloy is mainly determined by the electrochemical effect and hydrogen evolution reaction of the β' precipitates. As the previous analysis, the potential of β' precipitates is slightly lower than that of the matrix, and β' precipitates dissolution (as shown in Fig. 6b) is the main localized corrosion mechanism. A large amount of β' precipitations are produced in T6-treated alloy, and the interlayer structure of β' phase increases the contact area between the Mg atoms and the RE atoms, making Mg atoms with more active chemical properties more susceptible to corrosion dissolution. The corrosion dissolution of the β' precipitates also can retard the cathodic hydrogen evolution reaction in polarization process (Fig. 4). From the corrosion morphologies shown in Fig. 6c, it is found that there are a great number of tiny corrosion pits on the surface of the T6-treated alloy. As the amount of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ is few and the size of the β' precipitates is in the order of nanometer, for the same immersion period, the pitting corrosion that occurred on the surface of the T6-treated GW103K alloy is light and shallow.

5 Conclusions

T4 and T6 heat treatments modified the as-cast microstructure of the GW103K alloy, which led to their different corrosion behaviors. The electrochemical effect of the different precipitates on the localized corrosion of the alloy can be used to describe different corrosion mechanisms.

1. The T4 heat treatment decreased the amount of skeleton-like $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase and precipitated

the cuboid-shaped phase. After 193-h artificial aging, a few of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase and a great number of directional β' phase precipitated in the alloy.

2. T4 and T6 treatments improved the corrosion resistance of the GW103K alloy in the as-cast condition. The results were supported by the polarization test, and the evolution of microstructure of GW103K alloy with different treatments affects the value of corrosion current density and the hydrogen evolution reaction of corrosion process. The morphology of localized corrosion of the alloys in different conditions was associated with the presence and electrochemical role of different precipitates. The $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phase and β' precipitates acted as micro-anodes during the corrosion of the GW103K alloys in different conditions.
3. The GW103K alloy in the as-cast condition was sensitive to deep pits, attributing to preferential corrosion of $\text{Mg}_{24}(\text{Gd}, \text{Y})_5$ phases which were located in the large areas of grain boundaries. The T4-treated alloy exhibited a typical morphology of pitting corrosion. For the T6 condition, the pits did not extend deeply as in the other two kinds of alloys because the nanometer β' precipitates corroded.

Acknowledgements This work was supported financially by the National Natural Science Foundation of China (No. 51531007), the Natural Science Foundation of Inner Mongolia (No. 2016MS0538) and the Research Fund of State Key Laboratory for Marine Corrosion and Protection of Luoyang Ship Material Research Institute (LSMRI) (No. KF160408). The authors are grateful to Dr. Ping Qiu for modification in English.

References

- [1] M.K. Kulekci, *Int. J. Adv. Manuf. Technol.* **39**, 851 (2008)
- [2] S.B. Shen, S. Cai, X.G. Bao, P. Xu, Y. Li, S. Jiang, G.H. Xu, *Chem. Eng. J.* **339**, 7 (2018)
- [3] X.R. Chen, F.K. Ning, J. Hou, Q.C. Le, Y. Tang, *Ultrason. Sonochem.* **40**, 433 (2018)
- [4] X.W. Liu, Y. Liu, B. Jin, Y. Lu, J. Lu, *J. Mater. Sci. Technol.* **33**, 224 (2017)
- [5] L.P. Zhong, Y.J. Wang, M. Gong, X.W. Zheng, J. Peng, *Mater. Charact.* **138**, 284 (2018)
- [6] D.F. Zhang, X. Chen, F.S. Pan, L.Y. Jiang, G.S. Hu, D.L. Yu, *Funct. Mater.* **45**, 05001 (2014)
- [7] R.L. Satet, M.J. Hoffmann, *J. Am. Ceram. Soc.* **88**, 2485 (2005)
- [8] Y.R. Wu, W.Y. Hu, L.X. Sun, *J. Phys. D: Appl. Phys.* **40**, 7584 (2007)
- [9] L.L. Tang, Y.H. Zhao, R.K. Islamgaliev, R.Z. Valiev, Y.T. Zhu, *J. Alloys Compd.* **721**, 577 (2017)
- [10] Y. Gao, Q.D. Wang, J.H. Gu, Y. Zhao, Y. Tong, J.Y. Kaneda, *J. Rare Earths* **26**, 298 (2008)
- [11] X.B. Liu, R.S. Chen, E.H. Han, *J. Alloys Compd.* **465**, 232 (2008)
- [12] S.Q. Liang, D.K. Guan, X.P. Tan, L. Chen, Y. Tang, *Mater. Sci. Eng., A* **528**, 1589 (2011)

- [13] Q. Wang, L. Xiao, W.C. Liu, H.H. Zhang, W.D. Cui, Z.Q. Li, G.H. Wu, *Mater. Sci. Eng., A* **705**, 402 (2017)
- [14] S.Q. Liang, D.K. Guan, L. Chen, Z.H. Gao, H.X. Tang, X.T. Tong, R. Xiao, *Mater. Des.* **32**, 361 (2011)
- [15] H. Liu, Y. Gao, J.Z. Liu, Y.M. Zhu, Y. Wang, J.F. Nie, *Acta Mater.* **61**, 453 (2013)
- [16] D.K. Xu, E.H. Han, Y.B. Xu, *Prog. Nat. Sci.-Mater.* **26**, 117 (2016)
- [17] Y.X. Li, D. Qiu, Y.H. Rong, M.X. Zhang, *Intermetallics* **40**, 45 (2013)
- [18] J.X. Zheng, Z. Li, L.D. Tan, X.S. Xu, R.C. Luo, B. Chen, *Mater. Character.* **117**, 76 (2016)
- [19] Y.C. Wan, H.C. Xiao, S.N. Jiang, B. Tang, C.M. Liu, Z.Y. Chen, L.W. Lu, *Mater. Sci. Eng., A* **617**, 243 (2014)
- [20] Y.W. Song, D.Y. Shan, E.H. Han, *J. Mater. Sci. Technol.* **33**, 945 (2017)
- [21] J.H. Liu, Y.W. Song, J.C. Chen, P. Chen, D.Y. Shan, E.H. Han, *Electrochim. Acta* **189**, 190 (2016)
- [22] L.M. Peng, J.W. Chang, X.W. Guo, A. Atrens, W.J. Ding, Y.H. Peng, *J. Appl. Electrochem.* **39**, 913 (2009)
- [23] S.Q. Liang, D.K. Guan, X.P. Tan, *Mater. Des.* **32**, 1194 (2011)
- [24] J.Z. Zhang, Z.X. Ma, D.F. Li, *Mater. Heat Treat.* **38**, 73 (2007)
- [25] K. Zhang, X.G. Li, Y.J. Li, M.L. Ma, *Trans. Nonferrous. Met. Soc. China* **18**, 12 (2008)
- [26] X.M. Zhang, Z.Y. Mu, Y.L. Deng, C.P. Tang, L.Q. Guan, *J. Sci. Technol.* **44**, 2223 (2013)
- [27] J. Zhao, J.P. Li, Y.C. Guo, Z. Yang, Y.M. Yang, M.X. Liang, *Rare Met. Mater. Eng.* **37**, 281 (2008)
- [28] L.Y. Wang, J. Huang, J. Dong, K. Feng, Y.X. Wu, P.K. Chu, *Mater. Character.* **118**, 486 (2016)
- [29] T. Honma, T. Ohkubo, K. Hono, S. Kamado, *Mater. Sci. Eng., A* **395**, 301 (2005)
- [30] C. Antion, P. Donnadieu, F. Perrard, A. Deschamps, C. Tassin, A. Pisch, *Acta Mater.* **51**, 5335 (2003)
- [31] J.X. Zheng, X.S. Xu, K.Y. Zhang, B. Chen, *Mater. Lett.* **152**, 287 (2015)
- [32] S.M. He, X.Q. Zeng, L.M. Peng, X. Gao, J.F. Nie, W.J. Ding, *J. Alloys Compd.* **421**, 309 (2006)