



The Special Role of Anodic Second Phases in the Micro-galvanic Corrosion of EW75 Mg Alloy



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ABSTRACT

It is well known that second phases act as micro-cathodes in the corrosion of traditional Mg alloys. However, the effect of second phases on the corrosion behavior of Mg-rare earth (RE) alloys is ambiguous in view of the second phases consisting of Mg and more active RE elements. The role of second phases in the corrosion of cast EW75 (Mg–5Y–7Gd–1Nd–0.5Zr) was studied by scanning electron microscopy (SEM) observations, Scanning Kelvin Probe Force Microscopy (SKPFM) analysis, immersion and electrochemical tests. It is found that the second phases in EW75 are more active than Mg matrix and preferentially dissolved at the initial corrosion stage. It indicates that the second phases act as micro-anodes, which are greatly different from the role of second phases in traditional Mg alloys.

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1. Introduction

As the lightest engineering metal, Mg and its alloys have been more and more attractive in automotive and aerospace industries [1]. However, the poor corrosion resistance severely restricts their widespread applications [2,3].

It is well known that second phases play a key role in the corrosion resistance of Mg alloys. As for the traditional Mg alloys such as Mg–Al and Mg–Zn systems, the discrete second phases consisting of Mg and more inert alloying elements are nobler than Mg matrix and act as micro-cathodes to accelerate the corrosion of Mg matrix [4–6]. Moreover, Song et al. [7] found that the continuous second phases may act as a barrier to inhibit the corrosion propagation in Mg matrix.

Presently, rare earth (RE) Mg alloys are popular because of their higher creep resistance and strength at high temperature [8–11]. Especially, it is found that the corrosion resistance of traditional Mg alloys such as AZ91 and AM60 is improved with addition of REs. It is attributed to the reasons as follows: (1) decrease potential difference between second phases and Mg matrix [12–14] by formation of more active second phases containing REs; (2) purify the melt by formation of intermetallic compounds with impurities; (3) form a more compact REs oxide film [15]. Besides the

addition of REs into the traditional Mg alloys, there exist another type of Mg-RE alloys which only contain pure magnesium and REs. In this type Mg-RE alloys the second phases consist of Mg and more active REs [3–17]. The electrochemical stability of these second phases in comparison with Mg matrix is ambiguous. Zhang et al. reported the cathodic role of second phases in Mg–5Y–7Gd–1Nd–0.5Zr just according to the corrosion morphology of 2 h immersion [18]. Birbilis et al. [16] reported the inert second phases in Mg-RE alloys (where RE=Ce, La, Nd) based on the comparison of the polarization curves of Mg-RE intermetallic compounds and pure Mg. These previous works are strongly influenced by the traditional opinion of the nobler second phases. There are not enough proofs to support the cathodic role of second phases in Mg-RE alloys. In our previous work, it was found that the second phases in Mg-RE alloys preferentially corrode, which is greatly different from the typical corrosion status. Thus, this work aims to clarify the role of second phases in Mg-RE alloys and further to disclose the influence of REs on the corrosion resistance.

2. Experimental details

Cast EW75 (Mg–5Y–7Gd–1Nd–0.5Zr) and pure Mg were used for this investigation. EW75 magnesium alloy, produced by General Research Institute for Nonferrous Metals, PR China, is composed of (wt.%) 7.04 Gd, 4.53 Y, 1.29 Nd, 0.49 Zr, and Mg balance. The chemical composition (wt.%) of pure Mg, produced by Shanxi Yinguang Huasheng Magnesium Co., Ltd., PR China, is

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0.01 Si, 0.01 Al, 0.0032 Fe, 0.0012Cu, 0.01 Mn, and Mg balance. For metallographic characterization, specimens were wet ground with water through successive grades of SiC abrasive papers from P320 to P5000, followed by polishing with 1 μm diamond paste. Specimens for corrosion morphology observation were immersed in the 3.5 wt.% NaCl solution for different time intervals. Corrosion products were removed by chromic acid solution consisting of $180\text{ g l}^{-1}\text{ CrO}_3$. Surface and cross-section morphologies were observed by a scanning electron microscopy (SEM; Phillips XL30FEG) with the acceleration voltage of 14 kV. Sputtering was not carried out because the corrosion products were removed before SEM tests. Chemical composition was analyzed by energy dispersive X-ray spectroscopy (EDX) elemental mapping. Volta potential distributions of EW75 were probed using a Scanning Kelvin Probe Force Microscope (SKPFM; Multimode 3D, Bruker Corporation) in work function mode. The probe used in SKPFM measurements was magnetic etched silicon probe (MESP) ($k = 2.8\text{ N/m}$, Bruker Corporation, CA, USA) with piezoelectric tube size of $125 \times 125 \times 5\ \mu\text{m}$. Prior to each experiment, the tip was

checked by performing a potential measurement on a gold reference sample. A dual scan mode was applied with tapping mode to obtain the surface topography signal and the cantilever to record the potential signal. The results were analyzed by NanoScope Analysis software. The specimens for Volta potential test were polished to 1 μm diamond paste and cleaned in an ultrasonic bath using ethanol [19]. Electrochemical measurements were conducted in 3.5 wt.% NaCl solution at room temperature ($25 \pm 1\ ^\circ\text{C}$) using a PARSTAT4000 electrochemistry test system (Princeton Applied Research, USA). A classical three-electrode cell was used with platinum as counter electrode, saturated calomel electrode SCE (+0.242 V vs SHE) as reference electrode and the samples with an exposed area of 1 cm^2 as working electrode. Polarization measurements started from -250 mV vs. OCP at a constant scan rate of 0.5 mV s^{-1} and terminated until a final current density of approximately 10 mA cm^{-2} . The scan frequency of Electrochemical Impedance Spectroscopy (EIS) ranged from 100 kHz to 10 mHz with a perturbation amplitude of 20 mV. The EIS spectra were fitted using the ZSimpWin 3.20 software. Initial delay

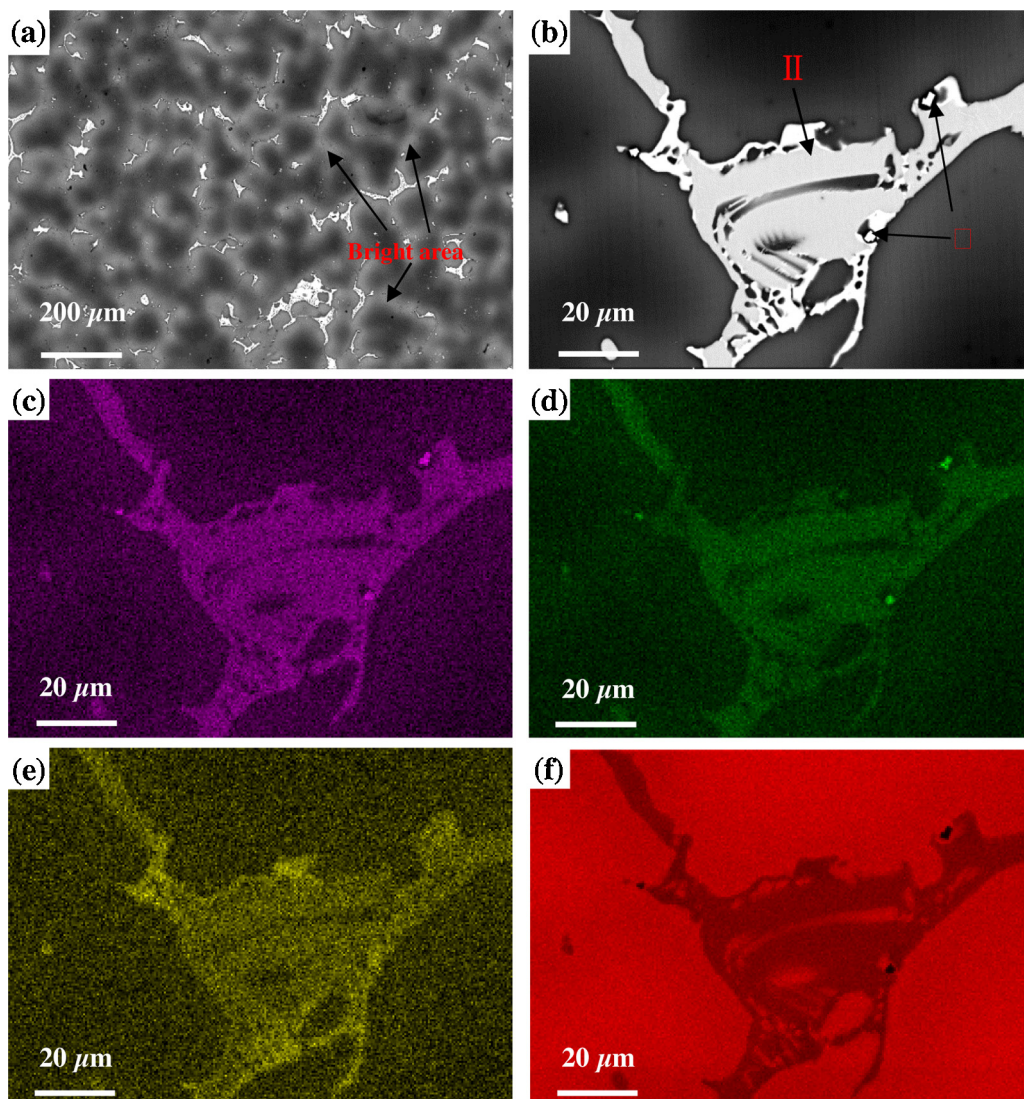


Fig. 1. BSE-SEM morphologies and EDX elemental mapping of cast EW75: (a, b) Surface morphologies; EDX elemental mapping of: (c) Gd, (d) Y, (e) Nd and (f) Mg.

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