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Effect of twins on the corrosion behavior of Mg–5Y–7Gd–1Nd–0.5Zr Mg alloy

Jinhui Liu [a, b], En–Hou Han [a, **], Yingwei Song [a, *], Dayong Shan [a]

[a] Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China
[b] School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China

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ABSTRACT

Deformation treatment is an efficient method to improve the mechanical properties of Mg alloys. However, twins inevitably arise during the deformation treatment due to the hexagonal closed–packed crystal structure of Mg. The role of twins in the corrosion behavior of Mg–5Y–7Gd–1Nd–0.5Zr (EW75) Mg alloy was studied by scanning electron microscopy (SEM) observations, scanning Kelvin probe force microscopy (SKPFM), zero–resistance ammeter (ZRA) measurements, scanning vibrating electrode technique (SVET), electrochemical tests and weight loss measurements. It is found that the micro–galvanic corrosion between twins and matrix plays the dual roles: accelerate the dissolution reaction of Mg substrate and promote the formation of surface film. The formation of compact surface film dominates the reactions in the EW75 alloy with twins. As a result, the twins in EW75 alloy can improve the corrosion resistance.

1. Introduction

Mg alloys are known as promising structural materials because of their many advantages, such as low density, and good specific strength and cast ability [1–5]. However, the yield and tensile strengths of cast Mg alloys are low. Deformation treatment is a suitable and effective method to improve their mechanical properties. However, abundant twins appear during the deformation due to the few slip systems in the hexagonal closed–packed (hcp) crystal structure of Mg [6–10]. These twins in the wrought Mg alloys have an effect on their corrosion behavior.

It has been reported the twins in AZ31 deteriorate the corrosion property of alloys [11,12]. However, Zou et al. reported that twinning could improve the corrosion resistance of Mg–Y alloys [13]. In this paper, the roles of twins in Mg–5Y–7Gd–1Nd–0.5Zr (EW75) Mg alloy have been detected. It is found that the appearance of twins improve the corrosion property as well. It seems that the twins play a different role in Mg–rare earth (Mg–RE) alloys in contrast to common Mg alloys without REs. However, the reason for this phenomenon is still unclear.

Wang et al. showed that the twinned areas in the {0002} oriented basal planes are mainly composed of {10–10} and {11–20} prism planes and the twinned areas in the {10–10} and {11–20} oriented prism planes can vary randomly [12]. That is, the crystallographic orientations of the twinned areas differ from the un–twinned areas in most cases. Song et al. and Pawar et al. reported the basal planes {0002} are more corrosion resistant than the prism planes {10–10} [14,15]. Thus, the micro–galvanic corrosion between twins and matrix would occur and accelerate the dissolution reaction of Mg substrate. Meanwhile, the micro–galvanic corrosion can promote the formation of the surface film. The interaction between the acceleration of dissolution and the promotion of surface film should be the key issue for the phenomenon that twins play a different role in Mg–RE alloys and common Mg alloys without REs. In this paper, the interaction would be discussed.

2. Experimental details

2.1. Material preparation and treatments

To avoid the influence of texture, cast EW75 was chosen as the raw material. Cast EW75 (Gd: 7.04 wt%, Y: 4.53 wt%, Nd: 1.29 wt%, Zr: 0.49 wt%, and Mg balance) was produced by the General Research Institute for Nonferrous Metals, PR China. The cast

* Corresponding author.
** Corresponding author.
E-mail addresses: ehhan@imr.ac.cn (E. Han), ywsong@imr.ac.cn (Y. Song).

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samples were solid–solution treated at 535 °C for 20 h (T4) in a muffle furnace, and then quenched into water at room temperature. The samples were wrapped up with Al foils during T4 treatment. After solution treatment, the samples were compressed with a strain rate of 10^{-3} s^{-1} and deformation ratio of 5 at room temperature (about 25 °C, T3) to obtain twins. In this article, the solid–solution treated samples without twins is denoted as T4 and the compressed sample with twins is denoted as T3. The residual stress in T3 sample was detected, and it was not so obvious that should be paid attention.

2.2. Microstructural analysis

The samples were wet ground with water through successive grades of SiC abrasive papers from P320 to P5000, polished with 1 μm diamond paste. The solution consisting of 4 mL of HNO_3 and 96 mL of ethanol was used for etch. The 3.5 wt% NaCl solution at room temperature was used for corrosion morphologies observation. The solution consisting of 180 g l^{-1} CrO_3 was used to remove corrosion products. Optical microscopy (OM, Carl Zeiss Axio Observer.Z1m) and scanning electron microscopy (SEM; Philips XL30FEG) equipped with an energy–dispersive X–ray spectroscopy (EDX) with an acceleration voltage of 14 kV were used for analysis.

2.3. Weight loss measurements

Samples for weight loss measurements were cut into coupons with dimensions of $25 \times 30 \times 10$ mm^3, ground to P2000, and weighed before exposure using a digital balance (Sartorius BSA2245–CW) with a precision of 0.0001 g as the original weight. After immersion for 7 d in the 3.5 wt% NaCl solution, the corroded specimens were immersed in a chromic acid solution for about 10 min to remove the corrosion products. Then, the specimens were washed with deionized water and dried by a hot air flow. Finally, the specimens were weighed to obtain the weight loss rate.

2.4. Scanning Kelvin probe force microscopy

Volta potential differences between twins and matrix of T3 sample were probed using a scanning Kelvin probe force microscope (SKPFM; Multimode 3D, Bruker Corporation) in work function mode. In work function mode, the lower Volta potential represents the higher activity. A dual scan mode was applied with tapping mode to obtain the surface topography signal and the potential signal. The specimens for SKPFM were polished to 1 mm diamond paste. The results were analyzed by Nano–Scope Analysis software.

2.5. Galvanic corrosion of the coupled T3 and T4 samples

To compare the corrosion behavior of T3 and T4 samples, two different techniques were used to detect the galvanic corrosion of the coupled T3 and T4 samples: zero–resistance ammeter (ZRA) and Scanning Vibrating Electrode Technique (SVET) measurements. 0.005 mol L^{-1} NaCl solution at room temperature was used as the corrosive medium for both measurements.

PARSTAT4000 electrochemistry test system (Princeton Applied Research, USA, P4000) was used for ZRA measurement. The samples were sealed in epoxy resin with an exposure area of 1 cm^2, and polished for the measurement. The T3 sample was connected to the working electrode (WE) and T4 was grounded. The galvanic current was measured every 5 s with a total duration of 2 h.

SVET equipment (Applicable Electronics Inc., USA) was controlled by the ASET 2.0 software (Science Wares Inc., USA). An insulated Pt/Ir probe (Microprobes Inc., USA), with platinum black deposited on a spherical tip of 15 μm diameter, was used as the vibrating electrode for the SVET system. Probe vibrations were ~30 μm in amplitude. The SVET scan height was fixed at 100 μm [16]. The T3 and T4 samples were sealed together using epoxy resin, and then polished for the SVET measurements. Since adjusting the probe to suitable sites of the SVET measurements spends about 30 min, the mapping could not be obtained until after immersion for 30 min.

2.6. Electrochemical tests

Electrochemical measurements were conducted using P4000 in 3.5 wt% NaCl solution at room temperature. A classical three–electrode cell was used, with platinum as the counter electrode, a saturated calomel electrode (SCE) (+0.242 V vs. standard hydrogen electrode) as the reference electrode, and the samples, sealed in epoxy resin with an exposure area of 1 cm^2, as the working electrode. Samples were ground to P2000. The anodic polarization scan started from the open circuit potential (OCP) and terminated at a final current density of approximately 10 mA cm^{-2}. The cathodic polarization scan started from the OCP and terminated at a potential of −250 mV vs. OCP. The scan rate was 0.5 mV s^{-1}. The scan frequency of electrochemical impedance spectroscopy (EIS) ranged from 100 kHz to 10 mHz with a perturbation amplitude of 10 mV rms. The EIS spectra were fitted using the ZSimpWin 3.20 software. An initial delay of 5 min was set for the polarization and EIS measurements to ensure a stable testing system.

All of the tests were repeated at least three times to ensure the accuracy.

3. Results

3.1. Microstructural characterization

The morphology of the T4 sample is shown in Fig. 1b. Compared with cast EW75 (Fig. 1a), less second phases can be found in the T4 sample. The remained second phases in the T4 sample exhibit two shapes, one is dot–shape (Fig. 1c) and the other one is cubic–shape (Fig. 1d). The dot–shape one is Zr particles and the cubic–shape consists of Mg, Y and Gd, which has been reported before [17–22].

The microstructures of the etched T3 and T4 samples are shown in Fig. 2. It can be found that second phases are negligible in two samples. Thus, the micro–galvanic corrosion between the second phases and Mg matrix in T3 and T4 samples is not discussed in the following research. Meanwhile, there is no strong texture in the T3 and T4 samples because they are sampled from the cast EW75 and T3 sample was compressed at the room temperature [23–25]. Also, the grain sizes of the T3 and T4 samples are similar (about 300 μm both of them). The most significant difference of the microstructure between the T3 and T4 samples is the existence of twins in the T3 sample.

3.2. Weight loss measurement

The weight loss results by immersion tests are shown in Fig. 3. The weight loss rates of the T3 and T4 samples are 1.32 and 2.03 mm y^{-1}, respectively, after immersion in 3.5 wt% NaCl solution for 7 d. The higher weight loss rate of the T4 sample proves that the corrosion resistance of T3 sample is better than T4 sample after a long term of immersion.