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Substantial corrosion resistance improvement in heat-treated Mg–Gd–Zn alloys with a long period stacking ordered structure

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HIGHLIGHTS

- LPSO phase are precipitated in Mg–15.24Gd–4.75Zn (wt.%) alloy by heat treatment.
- The LPSO phase can act as an anode during micro-galvanic corrosion with W-phase.
- LPSO phase can act as corrosion barrier and prevent penetration of corrosive ions.
- Samples with LPSO phase display considerably improved corrosion resistance.

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ABSTRACT

The microstructure and corrosion behaviors of Mg–15.24Gd–4.75Zn (in wt.%) alloy exposed to 3.5 wt% NaCl solution were investigated under as-cast, solution (T4), and aging-treated (T6 and T6F) conditions. Results show that the LPSO phase is absent in as-cast and T4-treated alloys but present in T6 and T6F alloys. All lamellar LPSO phases are distributed in α-Mg intragrains, which separates the matrix from the eutectic phase. The lamellar LPSO phase can act as a corrosion barrier, and protect the matrix from being easily corroded by decreasing the surface area of the matrix exposed to the NaCl solution at early stages of corrosion. The LPSO phase can also act as an anode during micro-galvanic corrosion with the W-phase, thereby protecting the matrix and restraining the cathodic reaction of hydrogen evolution. The interior of the LPSO phase can further prevent penetration of corrosive ions during subsequent corrosion processes. Thus, samples with the LPSO phase display uniform corrosion morphologies and considerably improved corrosion resistance.

1. Introduction

In recent years, the strength and ductility of Mg alloys have been remarkably improved by the discovery of long period stacking ordered (LPSO) structures [1–5]. Kawamura et al. [6] studied the LPSO structure in Mg–Gd–Zn alloys and considered these materials type II alloys; in this work, the LPSO phase was absent in as-cast ingots but precipitated during soaking at 773K. More recent studies, however, show that the LPSO phase exists in as-cast Mg–Gd–Zn alloys [7,8]. The β-phase in Mg–Gd–Zn alloys can transform into the LPSO phase, which is mainly distributed at grain boundaries [5]. Precipitation from the supersaturated matrix can also form the LPSO phase, which is distributed both at the grain boundaries and within the grains [9].

Unfortunately, most research works focus on the effect of the LPSO phase on the mechanical properties of the resultant material and ignore the corrosion behavior of the final alloys. Moreover, the poor corrosion resistance of Mg alloys seriously limits their application in engineering. Few articles have reported the corrosion behavior of Mg–Gd–Zn alloys. Zhang [10] reported that as-extruded Mg–11.3Gd–2.5Zn–0.7Zr (wt.%) alloy with a lamellar LPSO phase exhibits better corrosion resistance and more uniform corrosion than Mg–10.2Gd–3.3Y–0.6Zr (wt.%) alloy, wherein the LPSO phase is absent. By contrast, A. Srinivasan's studies [8,11] revealed that the lamellar LPSO phase facilitates filiform corrosion of Mg–10Gd–xZn ($x = 2$, and 6 wt%) alloys. Zhang [7] revealed

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that the lamellar LPSO structure along the grain boundary in as-cast Mg–5Gd–1Zn–0.6Zr (wt.%) alloy can act as a barrier between the substrate and the eutectic phase and inhibit galvanic corrosion.

The function of the LPSO phase on the corrosion resistance of the Mg–Gd–Zn alloys appears unclear, especially when the LPSO phase is precipitated from a supersaturated matrix. In the present study, a Mg–15.24Gd–4.75Zn (wt.%) alloy was prepared. The LPSO structure was absent in the as-cast alloy but appeared after heat treatment. The corrosion behaviors of the as-cast alloy without the LPSO phase as well as that of heat-treated alloys with the LPSO phase are extensively investigated.

2. Experimental procedures

2.1. Material preparation

An as-cast Mg–15.24Gd–4.75Zn (in wt.%) alloy ingot was prepared in an induction furnace under an inert Ar atmosphere and using high-purity ingots of Mg (99.95 wt%), Zn (99.99 wt%), and Mg–30 wt%Gd master alloy. Heat treatments were carried out at 540 °C for 4 h (T4), at 540 °C for 4 h with subsequent aging at 450 °C for 10 h (T6), and at 540 °C for 4 h with furnace cooling (T6F). The treated samples were then quenched with water at room temperature. Samples for microstructural characterization, electrochemical measurements, and immersion tests were prepared from the ingot and treated pieces. Each sample was successively ground to 1000 grit emery paper, degreased with acetone, rinsed ultrasonically in distilled water, and dried in cold air.

2.2. Microstructure analysis

Samples for microstructural observation were polished and etched using an oxalic acid solution [12]. Microstructures were observed using scanning electron microscope (SEM, VegaIILMU) equipment with an energy dispersive X-ray spectrometer (EDS). For phase analysis, X-ray diffraction (XRD, Rigaku D/MAX-2500PC) with Cu Kα radiation was performed, and MDI Jade 5.0 software was used to analyze the obtained XRD patterns. The detailed microstructures of LPSO phase in the samples were analyzed using transmission electron microscopy (TEM, Zeiss Libra 200 FE) at an accelerating voltage of 200 kV.

2.3. Electrochemical measurements

Electrochemical measurements were carried out at room temperature in 3.5 wt% NaCl solution. Samples were used as working electrodes and mounted in epoxy resin with an exposure area of 0.785 cm^2 (Φ 10 mm). A platinum plate and a saturated calomel electrode were respectively used as the counter and reference electrodes. Prior to potentiodynamic polarization testing, the open circuit potential of the alloys was measured for a minimum of 20 min to establish an approximately steady state, after which the polarization curve was measured at a constant scan rate of 1 mV/s. CorrView software was used to fit the polarization curves in R_p mode.

2.4. Immersion tests

To obtain the corrosion rate, immersion tests were performed in 3.5 wt% NaCl solution at 25 ± 1 °C in an air-conditioned room. Samples with dimensions of 10 mm × 10 mm × 3 mm were polished, cleaned, and dried. Hydrogen evolution was monitored to evaluate the corrosion rate of alloys in accordance with Ref. [13]. After 72 h of immersion, the samples were removed from the NaCl solution, gently rinsed with distilled water, and dried in cold air. Short-term immersion for 1 h was conducted to observe the corrosion characteristics of the samples. Corrosion products were removed using 200 g/L of chromic acid and 10 g/L of $AgNO_3$ for 10 min, after which surface morphologies were observed using SEM. After 27 h of hydrogen gas collection, the hydrogen evolution rate, V_H (mL/cm^2/d), was converted to corrosion rate according to the formula CR (mm/y) = 2.279 V_H (mL/cm^2/d) [13].

3. Results

3.1. Microstructural analysis

Backscattered images of the investigated alloys are shown in Fig. 1. The as-cast alloy consisted of primary α-Mg and white secondary phases, which form a network structure (Fig. 1a). The morphology of the alloys changed during heat treatment. T4 treatment dissolved most of the secondary phases and resulted in a supersaturated α-Mg phase, although some residual enlarged secondary phases were still observed (Fig. 1b). The percentage of the secondary phase area of Fig. 1a and b was measured through software Image pro plus. The results show the percentage of Fig. 1a is 19.68% and that of Fig. 1b is 18.74%. During T6 treatment, secondary phases at the grain boundaries and intragranular spherical particles appeared unchanged, but a fine lamellar phase precipitated within the grain (Fig. 1c). In the T6F-treated alloy (Fig. 1d), the grain boundary presented a eutectic structure, and the intragranular lamellar phase was easier to distinguish compared with the T6-treated alloy.

EDS results (Table 1) reveal that the atom ratios of Zn to Gd in the as-cast, T4-treated, T6-treated, and T6F-treated alloys are 1.85, 1.22, 1.40, and 1.50, respectively; these results confirm that all of the white phases in the alloys with and without heat treatment are $(Mg, Zn)_3Gd$ (W-phase). In addition, the lamellae formed within the T6-treated alloy contained 0.90 at.% Zn and 1.03 at.% Gd, whereas the lamellae formed in the T6F-treated alloy included 0.50 at.% Zn and 1.23 at.% Gd. The XRD pattern (Fig. 2) demonstrates that the lamellae observed are the LPSO phase; this phase has also been found in as-cast Mg–5Gd–1Zn–0.6Zr (wt.%) [7] and as-cast Mg–10Gd–*x*Zn ($x = 2$, and 6 wt%) alloys [8]. Zhang [7] found that LPSO phases distributed along the grain boundary disappear after T4 treatment at 535 °C for 12 h because of sufficient atomic diffusion. In the present study, the LPSO phase, which is absent in the as-cast state, precipitated within the grains because of atomic diffusion during the aging process.

TEM images of the lamellar phases in T6-treated and T6F-treated alloys are shown in Fig. 3. The bright field TEM images in Fig. 3a and c shows lamellar LPSO phases in the T6-treated and T6F-treated alloys; these phases may be clearly observed in the SEM image in Fig. 1 and correspond to the areas marked as D and F, respectively. The corresponding SAED patterns in Fig. 3b and d, which were obtained with the incident beam parallel to the [2110] direction of the HCP Mg matrix, indicate very weak spots located at positions of $n/14$ (where n is an integer) of the (0002) α-Mg diffraction. This finding reveals that lamellar LPSO phases in the T6-treated and T6F-treated alloys are 14H-type LPSO phases. The bright field TEM images further demonstrate that the lamellar LPSO phases in the T6F-treated alloy are long and thick whereas the LPSO phases in the T6-treated alloy are discontinuous.

The spaces of the LPSO phase in the T6F-treated alloy are wide whereas those in the T6-treated alloy are fairly dense. Similar results could also be seen in the SEM images in Fig. 1c and d.

3.2. Corrosion tests

The potentiodynamic polarization curves of the as-cast, and