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Full length article

Microstructure and corrosion behavior of Mg−Zn−Y−Al alloys with long-period stacking ordered structures

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Abstract

$Mg_{97-x}Zn_1Y_2Al_x$ alloys with long-period stacking ordered (LPSO) structures were prepared by conventional casting method. The optical microscopy (OM), X-ray diffraction (XRD) and the scanning electron microscope (SEM) equipped with energy dispersive X-ray spectroscopy (EDS) were used to analyze the microstructure of the alloys with different compositions. Immersion test and electrochemical measurement were used to evaluate the corrosion behavior of the alloys at room temperature, and the corrosive medium is 3.5% NaCl aqueous solution. The results showed that, with the increasing aluminum (Al) addition, except α-Mg and LPSO phases, new phases also emerged on the grain boundaries. At the same time, the zigzag part of LPSO phases disappeared, and the boundaries between LPSO phases and α-Mg became smooth. Furthermore, the addition of Al to Mg−Zn−Y alloys could hinder the activity of cathodic hydrogen evolution reaction and improve the uniformity and compactness of the protective surface film, thus, enhanced the corrosion resistance of Mg−Zn−Y alloys.

Keywords: Magnesium alloy; Rare earth element; SEM; XRD; Weight loss; Polarization

1. Introduction

Magnesium (Mg) alloys have become one of the potential engineer materials for automobile and aeronautical industries because of its high strength weight ratio and low density [1,2]. In order to obtain excellent properties and wide applications, many researchers have paid great attention to explore effective strengthening phases in Mg alloys [3,4]. During the last decades, the Mg−Zn−RE Mg alloy consists of α-Mg and long-period stacking ordered (LPSO, X phase) phases have been developed, alloys with this structure own unique microstructure and excellent mechanical properties [5,6]. The application of rapid solidification/power metallurgy processing to $Mg_{97}Zn_1Y_2$ alloy which can form LPSO phases in the alloy results in excellent yield strength (610 MPa) and elongation (5%), respectively [7,8]. The most important is that this long-period stacking ordered structure can also be obtained in conventional copper mold casting [9]. Furthermore, it is suggested that, LPSO phases also emerge in Mg−RE−X (X = Ag, Cu, Ni) alloys [10−13]. However, the corrosion behavior of LPSO-containing alloys and the effect of fourth element addition on corrosion behavior of Mg−Zn−RE alloys have not been investigated.

Al is one of the common elements in Mg alloys, in general, the addition of Al can improve the stability of protective film

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formed on the corroded Mg alloy surface, which in turn enhanced corrosion resistance [14,15]. Recent years, Yamasaki has investigated the corrosion behavior of LPSO Mg–Zn–Y alloys containing Al, which was fabricated by rapid solidification/power metallurgy processing [16]. The result showed that, due to the existence of Al which can modify the composition and structure of surface films, corrosion resistance of Mg–Zn–Y–Al alloys was increased with the increase of Al. However, the investigation of Al-containing Mg–Zn–Y LPSO phase alloys were prepared by conventional casting method was not reported, therefore, the investigation of effect of Al addition on microstructure and corrosion behavior of Mg–Zn–Y alloy provide a reference for the application of Mg–Zn–Y LPSO phase alloy.

2. Experimental

The alloys used for this investigation were prepared by well type crucible resistance furnace from high purity Mg (99.9%), Y (99.9%), Zn (99.9%) and Al (99.9%) in a shielding gas $CH_2FCF_3 + N_2$ atmosphere at 1033 K. In order to reduce the influence of impurity on the corrosion property, the melted alloy was refined at the last step of the melting process. Then it was cast into a preheated iron mold. The chemical compositions of Mg–Zn–Y–Al alloys are listed as follows in Table 1. The prepared $Mg_{97-x}Zn_1Y_2Al_x$ ingots were cut into cylinder-shaped specimens of φ30 mm × 3 mm. Specimens for immersion and polarization curve tests were ground to a 2000 grit SiC paper, and subsequently rinsed with absolute alcohol in an ultrasonic bath and dried in warm air. Specimens for metallographic observation were further ground to 3000 grit SiC paper, and then etched by 3% nital.

The immersion test was carried out at room temperature in 3.5% NaCl solution for 40 h. Prior to immersion test, the every surface of specimens was ground with 2000 grit paper, ultrasonically cleaned in acetone and dried with warm air. At the end of the test, they were immersed into 200 g/L CrO_3 + 10 g/L $AgNO_3$ boiling solution to remove the corrosion products attached on the specimen surface, then washed with distilled water and dried with hot air. The weighted mass changes of these specimens were measured on a one over ten-thousand analytical balance, and mass changes per unit of surface area were calculated to evaluate the corrosion resistance.

The polarization curves were measured using Land CS350 electrochemical system in 3.5% NaCl aqueous solution at room temperature. A classical three-electrode cell was used with a platinum as counter electrode, a saturated calomel electrode as reference electrode and the samples sealed by resin with an exposed area of 1 cm^2 as working electrodes. The working surfaces of the working electrodes for the test were ground using 2000 grit SiC paper and cleaned in acetone before exposed to the solution. After open-circuit potentials (OCP) was measured in 3.5% NaCl aqueous solution for 300 s at room temperature, polarization curves test was conducted at a scan rate of 2 mV/s.

The surface morphologies were observed with JSU-6700F scanning electron microscope (SEM) to determine the distribution and morphology of the phases on the surfaces of Mg–Zn–Y–Al alloys. The chemical compositions of different phases in Mg–Zn–Y–Al alloys were analyzed by an energy dispersive spectroscopy (EDS). Phase constitution analyses were performed with a Y-2000 X-ray diffractometer, using monochromatic Cu-Kα radiation.

Table 1
The chemical compositions of experimental alloys (wt.%).

Alloy	Chemical compositions (wt.%)			
	Mg	Zn	Y	Al
$Mg_{96.9}Zn_1Y_2Al_{0.1}$	90.63	2.39	6.85	0.13
$Mg_{96.8}Zn_1Y_2Al_{0.2}$	90.23	2.42	7.13	0.22
$Mg_{96.7}Zn_1Y_2Al_{0.3}$	90.11	2.45	7.10	0.34
$Mg_{96.5}Zn_1Y_2Al_{0.5}$	90.10	2.46	6.91	0.53
$Mg_{96}Zn_1Y_2Al_{1.0}$	89.45	2.53	6.88	1.14

3. Results and discussion

3.1. Microstructure

The microstructures of the Mg–Zn–Y–Al alloys are shown in Fig. 1. Combining with XRD study (as seen in Fig. 2), $Mg_{96.9}Zn_1Y_2Al_{0.1}$ and $Mg_{96.8}Zn_1Y_2Al_{0.2}$ alloys have similar microstructures compared with $Mg_{96.7}Zn_1Y_2Al_{0.3}$ alloy, therefore, the SEM images of alloys $Mg_{96.7}Zn_1Y_2Al_{0.3}$, $Mg_{96.5}Zn_1Y_2Al_{0.5}$ and $Mg_{96}Zn_1Y_2Al_1$ were selected to show the microstructure of Mg–Zn–Y–Al alloys. It can be seen in Fig. 1b, besides α-Mg phase and X phase, a small amount of strip-shaped phases can be observed in $Mg_{96.7}Zn_1Y_2Al_{0.3}$ alloy, and these strip-shaped phases primarily precipitated on the grain boundaries. When continued to increase the content of Al, the amount of strip-shaped phases increased, as shown in Fig. 1c, and had a trend to get together. Then, the amount of these clustered strip-shaped phases increased in the $Mg_{96}Zn_1Y_2Al_1$ alloy, as shown in Fig. 1d. Moreover, the morphology of X phase in the alloys changed with the increase of Al, the characteristic of the X phase from zigzag to smooth. It suggested that the formation of X phase based on atom diffusion [17] and the addition of Al could promote the diffusion of Zn and Y into grain boundary which was important for formation of X phase, but Al, simultaneously, consumed the Zn and Y by formed strip-shaped phases, thus, X phase became smooth and fine when increased the addition of Al. Fig. 1e and f shows the TEM image and SAED patterns of the X phase. In the SAED patterns, the spots were arranged in positions that divided the height between the incident beam and the $(0002)_{Mg}$ 6-fold. Based on the XRD peaks in Fig. 2 and SAED patterns in Fig. 1f, the X phase was determined as $Mg_{12}ZnY$, and had 18R LPSO structure which had been investigated by the previous study [18]. The composition of the strip-shaped phase was determined as $Mg_4Y_2ZnAl_3$ by EDS (Fig. 3). And the new peaks compared to the $Mg_{97}Zn_1Y_2$ alloy in XRD patterns also proved the existence of the new phases which were named as $Mg_4Y_2ZnAl_3$ in this paper.

The EDS spectra of α-Mg phase and X phase in the Mg–Zn–Y–Al alloys were shown in Tables 2 and 3,