



Full length article

Corrosion behavior of Mg–5Al based magnesium alloy with 1 wt.% Sn, Mn and Zn additions in 3.5 wt.% NaCl solution

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Abstract

The corrosion properties of four Mg–5Al alloys with M-alloying elements (tin, manganese and zinc) in a 3.5 wt.% NaCl solution were examined using electrochemical tests and surface analyses. The electrochemical results indicated that the addition of 1 wt.% M metal decreased the corrosion rate and hydrogen evolution rate of the Mg–5Al specimens. Moreover, the addition of 1Zn resulted in having the best corrosion resistance due to the interaction of Zn oxide with Mg and Al oxides which acted as a corrosion barrier.

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Keywords: Magnesium alloy; Alloying elements; Electrochemistry; Corrosion resistance

1. Introduction

Magnesium and its alloys are being attractive for employment in the fields like aerospace, electronic and automobile industries [1–3] for weight reduction and higher fuel efficiency. Unfortunately, magnesium alloys have limited corrosion resistance, which restricts their use in many industrial applications. When exposed to the environment, the poor corrosion resistance and low formability can result in material failure. Therefore, the demands for improved alloys with increased corrosion resistant properties and acceptable deformability at relatively low costs are ever-increasing to serve better and sustain future industry [4–8]. The general approach for this is

the addition of alloying elements. The most prevalently used are those which are more active elements and with reduction potentials similar to Mg, such as Al, Ca, Sr, etc. [9–15].

Al improves the corrosion resistance of Mg alloys due to the fact that Mg and Al form intermetallic compounds [16–19], $Mg_{17}Al_{12}$. Furthermore, Al-containing Mg alloys feature a thinner film with a density that increases with increasing Al content. The surface film of Al-containing alloys contains a mixture of MgO and Al_2O_3 or $Mg(OH)_2$ and $Al(OH)_3$. The presence of Al in the passive layer ameliorates its protective behavior [20–23]. But, the effect of small addition amount (such as 5 wt.%) of aluminum in the Mg alloy is still questionable as the corrosion resistance of Mg alloys is improved only at higher Al concentrations.

The aim of this study was to improve the corrosion resistance of Mg–5Al alloys by adding a small amount of M (M are tin (Sn) or manganese (Mn) or zinc (Zn)), which can improve the corrosion resistance of Mg–5Al alloys. The microstructure and electrochemical properties of the Mg–5Al alloy containing the M were evaluated. The effects of M addition on the structure and electrochemical properties were examined in detail.

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2. Experimental

Pure Mg (99.9%) ingot was melted in a stainless steel crucible under the protection of gas mixture containing SF_6 and CO_2 . The calculated amounts of 1.0 wt.% Sn, Mn, and Zn were added to Mg melt. After solidification, the ingots were subjected to homogenizing treatment at 400 °C for 12 h. The homogenized ingots were machined, which were used as raw materials for extrusion. The extrusion of billets was performed at 320 °C. The chemical compositions of alloys were determined by optical emission spectroscopy. Alloys with chemical compositions were 5.000 Al, 0.005 Si, 0.004 Fe, 0.003 Cu, 0.007 Ni, while the difference between measured and added composition of Sn, Mn, and Zn is imperceptible. The specimens for electrochemical tests were finished by grinding with 600-grit silicon carbide paper.

All of the electrochemical experiments were performed at room temperature in 3.5 wt.% NaCl solution. The exposed area was 1 cm². Potentiodynamic polarization tests were performed using an EG&G PAR 263A potentiostat for the DC measurements. A graphite counter electrode was used, with a saturated calomel electrode as the reference. Prior to the potentiodynamic polarization test, the samples were immersed in the solution for 1 h in order to stabilize the open-circuit potential. The potential of the electrodes was swept at a rate 0.166 mV/s in the range from the initial potential of −250 mV versus E_{corr} to the final potential of −1.3 V_{SCE}. The electrochemical impedance spectroscopy (EIS) and corrosion potential measurements were conducted using a IM6e system with a commercial software program for the AC measurements. The amplitude of the sinusoidal perturbation was 10 mV. The frequency range was from 100 kHz to 10 mHz. The hydrogen evolution of the alloys was investigated by immersion tests. The specimens, with dimensions of 10 mm × 10 mm × 2 mm, were prepared by grinding each side with 600 grid emery paper and degreasing the surfaces with ethanol prior to corrosion testing. The hydrogen evolution was used as an indicator of the corrosion rate, which was monitored every 1 h. To ensure reproducibility, at least three measurements were run for each specimen.

The crystal structure of the as-received specimens was investigated by XRD using Cu K α radiation. For the observation of the microstructure using optical microscopy, the specimens were mechanically abrasive with sand paper (#220, 600, 1200, 2000, and 4000) and then with 0.1 μm alumina powders. These specimens were then etched in a mixture of acetic acid (10 ml), picric acid (5 g), distilled water (10 ml) and ethanol (70 ml of 95% purity). The surface products were examined by X-ray photoelectron spectroscopy (XPS) after 1 h of the open-circuit potential.

3. Results and discussions

XRD patterns of the Mg–5Al–1M specimens are shown in Fig. 1. There is no significant difference in the α -Mg peaks between the Mg–5Al and M-containing specimens. The results also indicate that the well-defined peaks from Mg and

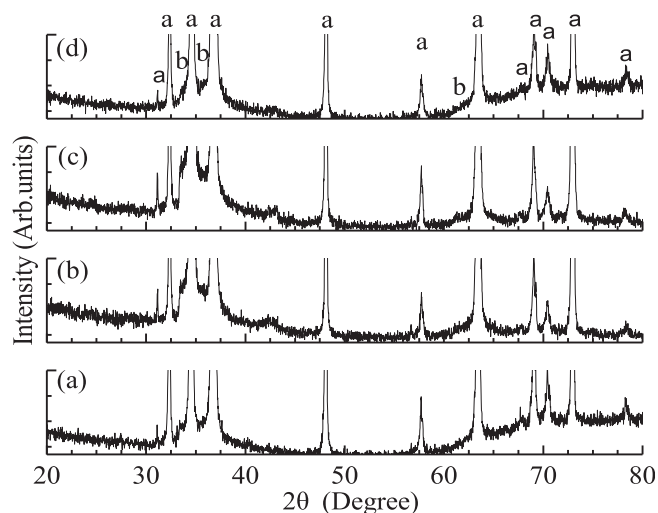


Fig. 1. XRD patterns of (a) Mg–5Al, (b) Mg–5Al–1Sn, (c) Mg–5Al–1Mn and (d) Mg–5Al–1Zn alloys: a, α -Mg and b, $\text{Mg}_{17}\text{Al}_{12}$.

$\text{Mg}_{17}\text{Al}_{12}$ reflections and no additional peak was observed. The microstructure included the primary α grains surrounded by new fine grains appearing at the grain boundary in the M-containing specimens due to recrystallization, as shown in Fig. 2. It indicates that the microstructure of the alloy is very different from Mg–5Al specimen and those containing M. The addition of M also decreased the grain size of the Mg–5Al alloy (8.29, 7.26, 5.23, and 3.30 μm for Mg–5Al, Mg–5Al–1Sn, Mg–5Al–1Mn, and Mg–5Al–1.0Zn, respectively).

Fig. 3 shows the polarization curves of the Mg–5Al–1M immersed in 3.5 wt.% NaCl solution. All specimens showed the active behavior where the anodic current increased with increasing potential. The potentiodynamic measurements showed that the M addition decreased the corrosion current density. This is because M additions hinder the cathodic hydrogen evolution reaction and shift the corrosion current densities toward the left site as shown in Fig. 3. This also accounts for the hydrogen activity and the uptake of hydrogen at the alloy surface which also decreases with the reduction in hydrogen evolution rate by M addition. Table 1 lists the corrosion properties. Where anodic and cathodic curves were near linear and symmetrical within ± 50 mV from E_{corr} , both Tafel slopes were extrapolated until the lines intersected at E_{corr} .

Fig. 4(a) and (b) present the Nyquist and Bode plots after immersion for 1 h at E_{corr} . The high spectra are used to detect the local surface defects, whereas the medium and low frequency spectra detect the processes within the corrosion product and at the metal/corrosion product interface, respectively. It was observed that the aperture of impedances and phase angles increased with M content due to the reduced hydrogen evolution rate, were as small aperture of impedance and phase angle were observed in the case of Mg–5Al specimen. This suggests that the addition of a small amount of 1 M promotes corrosion product formation. The corresponding equivalent circuit is given in Fig. 4(c), where R_s , CPE, R_c , C_c

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