Corrosion Properties and Microstructure of a Broad Range of Ce Additions on Mg–Zn Alloy

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To launch a new class of Mg alloys based on the Mg–Zn system, the effect of microstructural evolution on the corrosion properties in Mg–Ce–Zn system has been investigated. The alloys were fabricated by using a vacuum induction melting method under an argon atmosphere. Potentiodynamic polarization and hydrogen evolution test were carried out in 3.5% NaCl solution of pH 7.2 at room temperature to evaluate the corrosion properties of Mg–Ce–Zn alloys. The main constituents in Mg₉₉Ce_{0.5}Zn_{0.5}, Mg₉₈Ce_{1.5}Zn_{0.5} and Mg₉₂Ce_{7.5}Zn_{0.5} alloys are α -Mg and Mg₁₂Ce phase. On the other hand, Mg₄₁Ce₅ and Mg₃Ce phases are present in Mg₈₈Ce_{11.5}Zn_{0.5} and Mg₈₆Ce_{13.5}Zn_{0.5}. Although Ce additions on Mg alloy could tend to ennoble the corrosion potential, the corrosion rate was increased with excessive Ce additions.

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1. Introduction

Because of their low density, high specific strength and stiffness, Mg alloys have become candidate materials for many applications in microelectronics and in the automobile and aerospace industries.^{1–3)} The Mg–Al system, such as AZ91D and AM60B, has been the basis of the most widely used for Mg casting alloys. Although they are widely used in automotive industry, their applications are limited to the parts operated at temperature below 120°C because they show poor creep resistance and large decrease in strength at elevated temperature due to the thermal instability of microstructure. Moreover, Mg is also well known as a very active metal and its alloys have a low corrosion resistance, resulting in restricted application of Mg alloys to exposure environment. Therefore, in order to be extensively used in the automobile industry it is very important to improve the elevated temperature properties and corrosion resistance of Mg alloys.

In order to enhance the corrosion resistance of Mg alloys, many intensive and extensive fundamental investigations have been carried out during the past decade.^{4–8)} Most of studies have focused on role of alloying elements on corrosion properties of Mg alloys. Especially, it was reported that the addition of rare earth elements (RE) to Mg alloys has favorable effects on the various properties.^{9–11)} Therefore, the mechanical and corrosion properties of Mg alloys with RE elements, i.e. Ce, La and Nd, have become an important issue. However, the effect of RE additions on these properties of Mg alloys is not completely understood.

Typically RE is extracted as misch-metals of various compositions, most commonly Ce, followed by La, with smaller amounts of Nd and Pr, etc. In the Mg–RE alloys there are many different phases that may form, which are common to each of the rare earths considered in this paper, such as the Mg₁₂RE, Mg₃RE or Mg₂RE phases. According to a Mg–Ce

binary phase diagram,¹²⁾ the maximum solubility of Ce in an α -Mg matrix is about 0.1 at% at 590°C and Mg₁₂Ce, Mg₄₁Ce₅, Mg₃Ce, Mg₂Ce and MgCe phases were formed with up to about 7.7, 10.9, 25, 33.3 and 50 at%Ce addition, respectively. Recently, Zhang *et al.* studied the stoichiometry of two intermetallic compounds, Mg₁₂Ce and Mg₄₁Ce₅, on synthesized and annealed alloys.¹³⁾ They suggested a new phase diagram which containing newly suggested intermetallic compounds such as Mg₁₁Ce and Mg₃₉Ce₅, but it needs to be more detailed study. Although Stoichiometry study on the binary compounds in the Mg–Ce system is sometimes tried, the effect of Mg–Ce intermetallic compounds on corrosion properties of Mg alloys is still unclear. In the present work, a broad range of Ce additions (0.5–13.5 at%) on Mg–Zn alloy has been investigated for evaluating their corrosion behavior. The aims of this study identify of the phases and evaluate the electrochemical behavior of a broad range of Mg–Ce–Zn alloys.

2. Experimental Procedure

Pure Mg (99.8%), pure Zn (99%) and Mg–22 mass%Ce master alloy were used in this study. The alloys were fabricated by using a vacuum induction melting method under an argon atmosphere. All materials investigated in the present study are listed in Table 1. Microstructural analysis was carried out using an optical microscope and scanning electron microscope (SEM; Hitachi S-4300) equipped with an energy dispersive X-ray spectrometer (EDS). And the phases were analyzed via X-ray diffraction (Rigaku, CN2301) using monochromatic CuK α radiation in as-cast state.

Potentiodynamic polarization test was carried out to easily understand the effects of microstructure on the corrosion resistance of the Mg–Ce–Zn alloys. The test was conducted in 3.5% NaCl solution of pH 7.2 at 25°C by using an Electrochemical Interface Solartron SI 1287. Platinum gauze (25 mm $\times$ 25 mm, 60 mesh) was used as a counter electrode, and an Ag/AgCl electrode (in saturated KCl) was used as a reference electrode. Polishing was carried out on samples

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Table 1 Nominal compositions of Mg–Ce–Zn alloys (mol%).

Alloys	Ce	Zn	Mg	Remarks
Mg ₉₉ Ce _{0.5} Zn _{0.5}	0.5	0.5	Bal.	Hypoeutectic alloy
Mg ₉₈ Ce _{1.5} Zn _{0.5}	1.5	0.5	Bal.	Hypoeutectic alloy
Mg ₉₂ Ce _{7.5} Zn _{0.5}	7.5	0.5	Bal.	Hypereutectic alloy
Mg ₈₈ Ce _{11.5} Zn _{0.5}	11.5	0.5	Bal.	Intermetallic
Mg ₈₆ Ce _{13.5} Zn _{0.5}	13.5	0.5	Bal.	Intermetallic

with SiC paper up to 600 grits before starting measurements. The experiments were done at least three times and the solutions were neither deaerated nor stirred. During electrochemical corrosion tests, electrode potential was measured at a scan rate of 0.2 mV/s from -0.3 V versus open circuit potential (OCP) to -0.8 V versus reference. For the hydrogen evolution measurements, rectangular samples with a dimension of $25 \times 12 \times 10$ mm were prepared. The samples were

Fig. 1 X-ray diffraction patterns of various Mg–Ce–Zn alloys.

Fig. 2 SEM micrographs of the (a) Mg₉₉Ce_{0.5}Zn_{0.5}, (b) Mg₉₈Ce_{1.5}Zn_{0.5}, (c) Mg₉₂Ce_{7.5}Zn_{0.5}, (d) Mg₈₈Ce_{11.5}Zn_{0.5} and (e) Mg₈₆Ce_{13.5}Zn_{0.5} alloys. The (f) shows the EDS spectrums of secondary phases in Figs. 2(a)–2(e).

Fig. 3 SEM micrographs of eutectic structure of (a) $\text{Mg}_{99}\text{Ce}_{0.5}\text{Zn}_{0.5}$, (b) $\text{Mg}_{98}\text{Ce}_{1.5}\text{Zn}_{0.5}$ and (c) $\text{Mg}_{92}\text{Ce}_{7.5}\text{Zn}_{0.5}$ alloys.

placed on a pyrex glass plate filling with 3.5% NaCl solution (pH 7.2) and a calibrated hydrogen collection tube was set up over the corroding sample. The volume of evolved hydrogen was measured every 30 min during 72 h and the corrosion rate was calculated in ml cm^{-2} .

3. Results and Discussion

3.1 Microstructure

Figure 1 shows the optical microscopic images of the $\text{Mg}_{99}\text{Ce}_{0.5}\text{Zn}_{0.5}$, $\text{Mg}_{98}\text{Ce}_{1.5}\text{Zn}_{0.5}$, $\text{Mg}_{92}\text{Ce}_{7.5}\text{Zn}_{0.5}$, $\text{Mg}_{88}\text{Ce}_{11.5}\text{Zn}_{0.5}$ and $\text{Mg}_{86}\text{Ce}_{13.5}\text{Zn}_{0.5}$ alloys. As shown in hypoeutectic and hypereutectic alloys of Figs. 1(a)–1(c), these alloys exhibited a typical dendritic structure. With the increase of Ce contents, the dendritic structures became more obvious. On the other hand, the microstructure of $\text{Mg}_{88}\text{Ce}_{11.5}\text{Zn}_{0.5}$ and $\text{Mg}_{86}\text{Ce}_{13.5}\text{Zn}_{0.5}$ alloys in Figs. 1(d) and 1(e) shows absolutely different images comparing with hypo- and hypereutectic alloys.

Figure 2 shows the SEM images and EDS spectrum of secondary phases in Mg–Ce–Zn alloys. SEM/EDS results indicate that the main constituents in $\text{Mg}_{99}\text{Ce}_{0.5}\text{Zn}_{0.5}$, $\text{Mg}_{98}\text{Ce}_{1.5}\text{Zn}_{0.5}$ and $\text{Mg}_{92}\text{Ce}_{7.5}\text{Zn}_{0.5}$ alloys are α -Mg and Mg_{12}Ce phase. On the other hand, $\text{Mg}_{41}\text{Ce}_5$ and Mg_3Ce phases are present in $\text{Mg}_{88}\text{Ce}_{11.5}\text{Zn}_{0.5}$ and $\text{Mg}_{86}\text{Ce}_{13.5}\text{Zn}_{0.5}$; $\text{Mg}_{41}\text{Ce}_5$ seems to have formed from a peritectic reaction of $\text{Mg}_3\text{Ce} + \text{L} \rightarrow \text{Mg}_{41}\text{Ce}_5$. On the other hand, neither Ce–Zn intermetallic nor the ternary phases were detected. Figure 3 shows the comparison of eutectic structure of $\text{Mg}_{99}\text{Ce}_{0.5}\text{Zn}_{0.5}$, $\text{Mg}_{98}\text{Ce}_{1.5}\text{Zn}_{0.5}$ and $\text{Mg}_{92}\text{Ce}_{7.5}\text{Zn}_{0.5}$ alloys. With increase of Ce additions, the size of eutectic phase was coarsened.

Fig. 4 Summary of potentiodynamic polarization test in 3.5% NaCl solution. Values are given for corrosion potential (E_{corr}) and corrosion rate (I_{corr}).

3.2 Corrosion properties

The results obtained from the two types of corrosion tests of Mg–Ce–Zn alloys are presented in Figs. 4 and 5, with the former for the polarization test and the latter for the hydrogen evolution test.

Potentiodynamic polarization tests were carried out in triplicate and summarized in Fig. 4. From the Fig. 4, we see the values for the corrosion potential (E_{corr}) and the corrosion rate (expressed in the form of corrosion current density, I_{corr}).

Fig. 5 Corrosion rates of Mg–Ce–Zn alloys as a function of immersion time.

for the alloys tested in 3.5% NaCl solution. The corrosion potential of Mg₉₉Ce_{0.5}Zn_{0.5}, Mg₉₈Ce_{1.5}Zn_{0.5}, Mg₉₂Ce_{7.5}Zn_{0.5}, Mg₈₈Ce_{11.5}Zn_{0.5} and Mg₈₆Ce_{13.5}Zn_{0.5} alloys was -1.52 , -1.49 , -1.44 , -1.40 and -1.39 , respectively. Results indicated that increasing Ce alloying addition leads to an increase of the corrosion potential by an amount of up to 30–130 mV. This suggests that the addition of Ce tends to ennoble the E_{corr} value of the Mg alloys. On the other hand, the value of I_{corr} was also increased with increasing of Ce additions. It suggests that the value of E_{corr} however—which may be of relevance should alloys be galvanically coupled—is not indicative of corrosion rate. This is already confirmed in our previous study and very clear. And a similar phenomenon was also reported in the other study.¹⁴⁾

Normally, the addition of RE (La, Ce and Nd) is believed to have a beneficial effect on the corrosion resistance of Mg alloys. Takenake *et al.* indicated that the small addition of RE has a beneficial effect on the corrosion properties but

Fig. 6 SEM micrographs of corroded surface after 10 min in 3.5% NaCl solution; (a) and (d) Mg₉₈Ce_{1.5}Zn_{0.5}, (b) and (e) Mg₉₂Ce_{7.5}Zn_{0.5} and (c) and (f) Mg₈₈Ce_{11.5}Zn_{0.5} alloys.

excessive RE addition deteriorates the corrosion resistance.¹¹⁾ In this work, excessive Ce additions seem to be caused to increase in corrosion rates. Hence it is clear that the RE additions on Mg alloys does not always associate with an improvement in corrosion resistance.

Figure 5 illustrates corrosion rates of a broad range of the Mg–Ce–Zn alloys immersed in 3.5% NaCl solution. The corrosion rates were increased with increasing of excessive Ce additions. And all of alloys show that the corrosion rate was steadily increased with increase of immersion time. In order to clear the influence of microstructural evolution on corrosion properties of Mg–Ce–Zn alloys, the SEM images of initial corrosion stage were described in Fig. 6. The initial corrosion stage of the samples is shown in Fig. 6. From the Figs. 6(a)–6(c), several regions with severe corrosion were observed due to the galvanic effect. Indeed, it is known that localized and galvanic corrosion is the most common form of corrosion for Mg alloys in chloride-containing solutions. The Mg–Ce–Zn alloys were also predominated over localized and galvanic corrosion.

In magnified images in Figs. 6(d)–6(f), the corrosion was initiated at interface of α -Mg/Mg₁₂Ce and Mg₄₁Ce₅/Mg₃Ce due to galvanic effect. It is reported that the corrosion potential of α -Mg and Mg₁₂Ce phase was known as -1.65 and -1.5 V_{SCE}, respectively.¹⁴⁾ But that of other phases, Mg₄₁Ce₅ and Mg₃Ce, are still unclear. The initial corrosion was preferentially occurred at α -Mg [in Fig. 6(d)] and Mg₃Ce [in Fig. 6(f)]. It is indicated that the Mg₁₂Ce phase has a higher galvanic potential than α -Mg and Mg₄₁Ce₅ phase has a higher galvanic potential than Mg₃Ce. From these results, it is postulated that the corrosion potential of Mg–Ce intermetallic compounds is increased with increasing of Ce additions.

4. Conclusions

In the present study, we have investigated the relationship between microstructural evolution and corrosion properties in Mg–Ce–Zn alloys. Major conclusions can be summarized as follows.

- (1) The Mg₉₉Ce_{0.5}Zn_{0.5}, Mg₉₈Ce_{1.5}Zn_{0.5}, and Mg₉₂Ce_{7.5}-Zn_{0.5} alloys mainly consisted of α -Mg and Mg₁₂Ce phases. With the increase of Ce contents, the volume

fraction of Mg₁₂Ce phase was increased. On the other hand, Mg₈₈Ce_{11.5}Zn_{0.5} and Mg₈₆Ce_{13.5}Zn_{0.5} alloys composed of Mg₄₁Ce₅ and Mg₃Ce phases.

- (2) Ce additions lead to an increase of the corrosion potential of Mg alloy. But the excessive Ce additions lead to increase of corrosion rate.
- (3) The main corrosion mechanism was confirmed as localized and galvanic corrosion.

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