Influence of Zn Addition on Aging Response and Corrosion Resistance of Mg-Gd-Nd-Zr Alloy

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The age hardening response and corrosion resistance of Mg-8%Gd-2%Nd-0.3%Zr alloys with various Zn contents up to 2% (in weight) have been investigated. The Zn-free alloy exhibits relatively lower age hardening and slower age response, whereas the addition of Zn enhances the age hardening response remarkably. The weight loss after salt spray test decreases with increasing Zn content in the peak-aged alloys, which is presumably associated with the increased amount of eutectic Mg-Zn-Nd-Gd phase acting as a corrosion barrier along the α grain boundaries. The potentiodynamic polarization curves reveal that with the increase in Zn content, the value of I_{corr} decreases gradually while the value of E_{corr} increases. [doi:10.2320/matertrans.MC200743]

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1. Introduction

Magnesium (Mg) alloys have gained increasing attention due to many superior characteristics and their demands on many applications such as automobile parts and mobile IT products. However, low mechanical properties of Mg alloys at elevated temperatures and relatively poor corrosion resistance have retarded their wider utilization.^{1,2)} Therefore, one of current critical aims for alloy development is to enhance both elevated temperature properties and corrosion resistance so that their application can be more diverse.³⁻⁵⁾ The additions of heavy metal rare-earth (RE) elements such as Y, Gd, Dy, Tb and Nd to Mg alloy have been known to bring excellent tensile and creep properties as well as corrosion resistance after proper peak-aging treatment.⁵⁻¹⁰⁾

Recently, it was found that Zn plays a beneficial role in accelerating age hardening response and increasing peak strength for binary Mg alloys containing RE elements, Sn or Ca because the Zn addition gives rise to uniform and dense distribution of basal precipitates.^{11,12)} In spite of many works on role of Zn in microstructure and mechanical properties up to date,¹³⁻²⁰⁾ the effect of Zn addition on the corrosion resistance of Mg-RE based alloys has been rarely investigated. In this study, the variations in age hardening response and corrosion resistance with Zn content were investigated and discussed for Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys.

2. Experimental

Four Mg-8%Gd-2%Nd-0.3%Zr-(0, 0.5, 1 and 2)%Zn (in weight) alloys were melted in a steel crucible under the protection of (SF₆ + CO₂) mixed gas and poured into the metallic mold that was preheated to 200°C. The chemical compositions of experimental alloys are listed in Table 1. The alloy ingots were cut into small pieces and solution-treated at 530° for 6 hrs, followed by a water quench at 80°C and aging at 220°C up to 72 hrs. In order to investigate the aging response characteristics, the micro-hardness of solution-treated and aged specimens was measured by using

Table 1 Chemical compositions of alloys used in this study (mass%).

Alloys	Gd	Nd	Zr	Zn	Mg
Mg-8%Gd-2%Nd-0.3%Zr	7.41	1.79	0.32	—	Bal.
Mg-8%Gd-2%Nd-0.3%Zr-0.5%Zn	7.65	1.94	0.32	0.52	Bal.
Mg-8%Gd-2%Nd-0.3%Zr-1%Zn	7.46	1.93	0.27	0.83	Bal.
Mg-8%Gd-2%Nd-0.3%Zr-2%Zn	7.53	1.95	0.27	1.86	Bal.

a Vickers micro-hardness tester under a load of 100 gf. Microstructural examinations were carried out by means of optical microscope (OM), field emission scanning electron microscope (FE-SEM) equipped with energy-dispersive X-ray spectrometer (EDX) and field emission transmission electron microscope (FE-TEM) operating at 200 kV.

The salt spray test was conducted according to the ASTM B117 standard; 5% NaCl solution, operation temperature of 35°C, humidity of 95%, test period of 72 hrs. The corrosion products were cleaned by a chromate acid solution of (180 g CrO₃ + 1 g AgNO₃/ℓ distilled water) at the ambient temperature for 5 min, and then the weight loss was calculated. On the other hand, the polarization curves were obtained in the electrolytic cell containing 5% NaCl solution during the electrochemical tests. The surface was sealed with epoxy resin except for the area of 1 cm diameter that was exposed for the test.

3. Results and Discussion

3.1 Microstructure

Figure 1 shows the age hardening curves of Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys at 220°C after solution treatment. The Mg-8%Gd-2%Nd-0.3%Zr alloy displayed the lowest peak hardness and the slowest age response among the experimental alloys. It is obvious that the time for peak hardness is decreased whereas the peak hardness value is increased with increasing Zn content. The relatively poor age response for the Zn-free alloy would be closely related to lower volume fraction and non-uniform distribution of the

Fig. 1 Change in Vickers hardness with aging time for Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys.

strengthening precipitates.¹¹⁾ Optical microstructures of the peak-aged Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys are represented in Fig. 2. It can be seen that the alloys are primarily composed of α -Mg matrix and some precipitates appear along the grain boundaries and within the grains. In view of previous reports,^{13,14)} the precipitates along the α grain boundaries may well be eutectic compounds which were not solutionized during the solution treatment and

precipitates gathered within the grains are Zr-containing particles. It is interesting to note that Zn-free alloy does not have eutectic phase along the grain boundaries (Fig. 2(a)), while the amount of eutectic phase along the grain boundaries becomes greater with the increase in Zn content (Figs. 2(b)–(d)). Furthermore, the addition of Zn affects to decrease the grain size (average grain sizes of the alloys are measured as 148 (0%Zn), 81 (0.5%Zn), 64 (1%Zn) and 56 μ m (2%Zn), respectively). Figure 3 shows the SEM images of (a) Mg-8%Gd-2%Nd-0.3%Zr and (b) Mg-8%Gd-2%Nd-0.3%Zr-2%Zn alloys. The EDX results indicate that the compounds observed at the grain boundaries for the Zn-free alloy (Fig. 3(a)) are Mg-Gd-Nd compound, whereas those for the 2%Zn-containing alloy (Fig. 3(b)) are Mg-Zn-Nd-Gd phase, respectively. TEM microstructures of the peak-aged Zn-free and 2%Zn-containing alloys are shown in Fig. 4. The precipitates with fine lenticular morphology were identified as Mg-Gd-Nd (Fig. 4(a)) and Mg-Zn-Nd-Gd (Fig. 4(b)), respectively, as observed in Fig. 3. We did not investigate the nano-sized fine precipitates such as β'' , β' or β phase within the grains, because previous works had already been done on precipitation process which is closely related to the age hardening for these alloy systems.^{14,15)}

3.2 Corrosion resistance

3.2.1 Salt spray test

The corrosion rates obtained after the salt spray tests for Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys in 5%NaCl for

Fig. 2 Optical microstructures of peak-aged (a) Mg-8%Gd-2%Nd-0.3%Zr, (b) Mg-8%Gd-2%Nd-0.3%Zr-0.5%Zn, (c) Mg-8%Gd-2%Nd-0.3%Zr-1%Zn and (d) Mg-8%Gd-2%Nd-0.3%Zr-2%Zn alloys.

Fig. 3 SEM images and EDX spectrum on the precipitates located at grain boundaries for peak-aged (a) Mg-8%Gd-2%Nd-0.3%Zr and (b) Mg-8%Gd-2%Nd-0.3%Zr-2%Zn alloys.

Fig. 4 TEM images of peak-aged (a) Mg-8%Gd-2%Nd-0.3%Zr and (b) Mg-8%Gd-2%Nd-0.3%Zr-2%Zn alloys.

72 hrs are given in Fig. 5. It is noteworthy that the corrosion rate decreases continuously from 3.94 to 1.53 mg/cm²/day by the addition of Zn up to 2%. The cross sectional microstructures of the corroded surface after the salt spray tests are represented in Fig. 6. All the investigated alloys exhibit corrosion pits along the grain boundaries. As observed in Fig. 6, the corrosion pits of Zn-free alloy are apparently larger and deeper than other Zn-containing alloys. Song *et al.* reported that in the case of AZ91 alloy, higher β fraction, usually formed along the grain boundaries, and

more continuous manner of β phase in response to finer α grains would give rise to better corrosion resistance of the alloy, because β networks can act as a corrosion barrier.²¹⁾ Considering the previous report²¹⁾ and Figs. 2, 3 and 6, the enhanced corrosion resistance during the salt spray test by the addition of Zn is thought to be closely associated with the higher volume fraction and more continuous manner of grain boundary Mg-Zn-Nd-Gd compounds resulting from grain refinement.

Fig. 5 Corrosion rates of peak-aged Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys after salt spray test.

3.2.2 Electrochemical corrosion test

Figure 7 and Table 2 demonstrate the typical polarization curves and the values of I_{corr} and E_{corr} of Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys. The polarization curves consist of cathodic and anodic reactions. The cathodic polarization curves are assumed to represent the cathodic hydrogen evolution through water reduction as reaction (1), while the anodic ones represent the dissolution of Mg as reaction (2):²¹⁾

The hydrogen evolution did not stop when the polarization potential increases to the anodic region due to the negative different effect (NDE).¹⁸⁾ On the other hand, it became even more intensive as the polarization potential increases to be more positive than the corrosion potential (E_{corr}). The values of I_{corr} of investigated alloys are gradually decreased with increasing Zn content whereas the values of E_{corr} are gradually increased. This result clearly indicates the enhanced corrosion resistance of the Zn-containing alloys.

4. Summary

The peak hardness for Mg-8%Gd-2%Nd-0.3%Zr alloys with different Zn contents can be obtained through isothermal aging at 220°C and the aging response time for the peak hardness is substantially reduced as the Zn content is increased.

The corrosion rate calculated by the salt spray test gradually decreases with increasing Zn content presumably because the precipitated compounds along the grain boundaries act as the corrosion barrier. In electrochemical corrosion tests the values of I_{corr} are gradually decreased with increasing Zn content whereas the values of E_{corr} are gradually increased, implying that the corrosion resistance is improved by Zn addition.

Fig. 6 Cross-sectional microstructures of the corroded surface after salt spray test for peak-aged (a) Mg-8%Gd-2%Nd-0.3%Zr, (b) Mg-8%Gd-2%Nd-0.3%Zr-0.5%Zn, (c) Mg-8%Gd-2%Nd-0.3%Zr-1%Zn and (d) Mg-8%Gd-2%Nd-0.3%Zr-2%Zn alloys.

Fig. 7 Typical polarization curves of peak-aged Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys.

Table 2 Values of I_{corr} and E_{corr} of peak-aged Mg-8%Gd-2%Nd-0.3%Zr-(0~2)%Zn alloys.

Alloys	$I_{\text{corr}} (\times 10^{-5} \text{ A/cm}^2)$	$E_{\text{corr}} (\text{V})$
Mg-8%Gd-2%Nd-0.3%Zr	3.43	-1.84
Mg-8%Gd-2%Nd-0.3%Zr-0.5%Zn	2.95	-1.79
Mg-8%Gd-2%Nd-0.3%Zr-1%Zn	2.62	-1.76
Mg-8%Gd-2%Nd-0.3%Zr-2%Zn	1.35	-1.73

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