



## Special Feature: Advanced Alloy Design and Processing of Metallic Materials for Weight- and Energy-saving of Automobiles

Research Report

### Improvement of Corrosion Resistance of Mg-9%Al Alloys Containing Copper by Zinc Addition

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**■ABSTRACT■** When magnesium alloys are separated and collected from used vehicles, and ingots are produced in the recycling process, copper contamination can easily occur, and can lead to a significant deterioration of corrosion resistance. In this study, to improve the corrosion resistance of AZ91 alloy containing copper, the microstructure and corrosion resistance of Mg-9%Al alloys containing copper and zinc were investigated, and the mechanism by which zinc improves the corrosion resistance was considered.

The corrosion resistance of Mg-9%Al alloy decreased with increasing copper content, but was significantly improved with increasing zinc content, particular 3% or higher. In the AZ91 alloy containing copper,  $\alpha$ -Mg,  $\beta$ -phase  $Mg_{17}Al_{12}$ , and  $Mg_6Al_7Cu_3$  were observed. With the addition of zinc, the  $Mg_6Al_7Cu_3$  changed to  $Mg_{32}(Al, Zn, Cu)_{49}$ . These copper-containing compounds are both considered to be cathodic, but the cathodic current density for  $Mg_{32}(Al, Zn, Cu)_{49}$  was found to be smaller than that for  $Mg_6Al_7Cu_3$ . This led to significantly improved corrosion resistance for the zinc containing alloy.

**■KEYWORDS■** Magnesium Alloy, AZ91 Alloy, Corrosion Resistance, Containing Copper, Adding Zinc, Polarization Curve

#### 1. Introduction

Reducing the weight of automobiles is important in terms of decreasing CO<sub>2</sub> emissions and protecting the global environment. Consequently, it is expected that lightweight materials such as aluminum (Al) and magnesium (Mg) alloys will find increased use. However, since there is also an environmental load associated with materials production, it is essential to efficiently recycle the materials used in a vehicle.

One problem with recycling is contamination by impurities. In the case of Mg alloys, which have the lowest densities of any metals in practical use, the corrosion resistance deteriorates significantly with increasing concentration of impurities such as iron (Fe), nickel (Ni), and copper (Cu).<sup>(1,2)</sup> In the case of Fe, the maximum amount that can be tolerated in Mg alloys is 50 ppm.<sup>(3)</sup> Fe enters Mg alloys from the Fe crucible in the remelting process during ingot production. However, most can be removed by adding manganese (Mn) to the molten Mg alloy because high-melting-point Al-Mn-Fe compounds are formed and settle to the bottom of the crucible.<sup>(4,5)</sup> In the case

of Ni, its solubility in the molten alloy is extremely small, so little mixing is expected during recycling.

The most commonly used Mg alloy is AZ91 with a composition of Mg-9%Al-0.7%Zn-0.3%Mn. If Cu enters AZ91, Mg-Al-Cu compounds are formed and the corrosion resistance of the alloy deteriorates significantly.<sup>(6)</sup> The maximum amount of Cu that can be present is 300 ppm.<sup>(3)</sup> However, no effective additive has been found for removing Cu in a similar manner to Fe removal by Mn.

It is thought that Cu can become easily mixed with Mg alloys from cast Al alloys and electrical wiring when Mg alloys are separated and collected from used vehicles, and ingots are produced in the recycling process. Thus, the most important problem with regard to recycling Mg alloys is to control the deterioration of corrosion resistance that occurs with increasing Cu content.

We previously found that zinc (Zn) was an effective additive element for achieving this. In the present study, to improve the corrosion resistance of AZ91 alloy containing Cu, the microstructure and corrosion resistance of Mg-9%Al alloys containing Cu and Zn

were investigated to determine the role of Zn.

## 2. Experimental Procedure

### 2.1 Evaluation of Corrosion Resistance and Observation of Microstructure

#### Samples

In the present study, Cu and Zn were added in various amounts to AZ91 to produce alloys with the compositions Mg-9%Al-(0-6)%Zn-(0-1)%Cu-0.3%Mn. Alloys containing more than 0.7% Zn were cast from commercial AZ91D ingots and grains of pure Zn and Cu. Alloys containing less than 0.7% Zn were cast from ingots of pure Mg and Al, Mg-3.3%Mn alloy ingots, and grains of pure Zn and Cu. These raw materials were melted at 1023 K and were subjected to high-pressure die casting. **Table 1** shows the casting conditions. Some alloys were cast using gravity casting with a steel die with dimensions of  $25 \times 35 \times 300 \text{ mm}^3$ . The chemical composition of the cast alloys was analyzed using X-ray fluorescence (XRF) spectroscopy.

#### Corrosion Test

Samples with dimensions of  $2 \times 25 \times 25 \text{ mm}^3$  were prepared for corrosion tests by cutting castings. They were polished with #600 waterproof abrasive paper and then washed with acetone. For the corrosion test, the samples were soaked in a 5% NaCl solution. For Mg alloys, corrosion involves the oxidation reaction  $\text{Mg} \rightarrow \text{Mg}^{2+} + 2\text{e}^-$  in anodic regions, and the reduction reaction  $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$  in cathodic regions.<sup>(7)</sup> Therefore, the weight loss due to corrosion can be

calculated by measuring the volume of the hydrogen bubbles produced in the solution during the 100-h corrosion test. The corrosion rate (*MCD*) was calculated by dividing the corrosion weight loss by the surface area of the sample and the time.

#### Observation of Microstructure

The microstructure of the cast alloys was observed by scanning electron microscopy (SEM) and electron microprobe analysis (EPMA). Compounds in the alloys were investigated by transmission electron microscopy (TEM) and selected area electron diffraction. Samples after corrosion tests were washed with a solution containing 15 g of chromic acid, 1 g of silver nitrate, and 100 ml of water, and corrosion products on their surface were removed. The surfaces were then observed by SEM.

### 2.2 Evaluation of Electrochemical Properties

To investigate their corrosion behavior, Mg-9%Al-(0.7, 3)%Zn-0.5%Cu-0.3%Mn alloys were dipped in a 5% NaCl solution and their potential was measured. **Table 2** shows the measurement conditions.

Polarization curves were measured for  $\alpha$ -Mg and Mg-9%Al-(0.7, 3)%Zn-0.5%Cu-0.3%Mn alloys. The phases present in the alloys were first identified by EPMA. The polarization curves were measured using the same experimental setup as that used to determine the potential. Anodic polarization curves were measured from the potential to +1.0 V at a sweep rate of 50 mV/min and a sampling interval of 0.5 s after immersing the sample in the 5% NaCl solution for 30 min. Cathodic polarization curves were measured from the potential to -0.4 V.

**Table 1** High-pressure die casting conditions.

Casting temperature	$T_L + 50 \text{ K}$
Shot velocity	0.4 m/s
Shot pressure	64 MPa
Mold temperature	R.T.
Shape of cavity	40-150-3 mm (Plate shape)

**Table 2** Polarization measurement conditions.

System	HZ-5000 HOKUTO DENKO
Reference electrode	Ag/AgCl
Counter electrode	Pt
Solution	5% NaCl
Measure time	30 min
Sampling interval	5 s

### 3. Results and Discussion

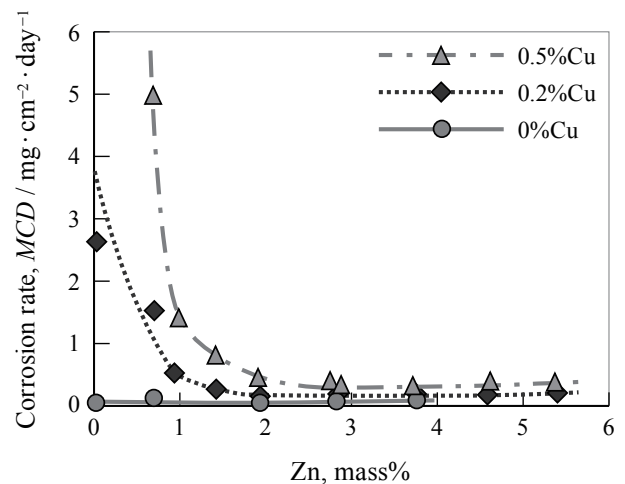
#### 3.1 Corrosion Resistance and Microstructure

**Figure 1** shows the dependence of the corrosion rate on the Cu content for high-pressure die-cast Mg-9%Al alloys with different amounts of Zn. The corrosion rate clearly increases with increasing Cu content, but this effect is suppressed by the presence of Zn. However, the beneficial effect of Zn appears to saturate at a Zn content of about 3%.

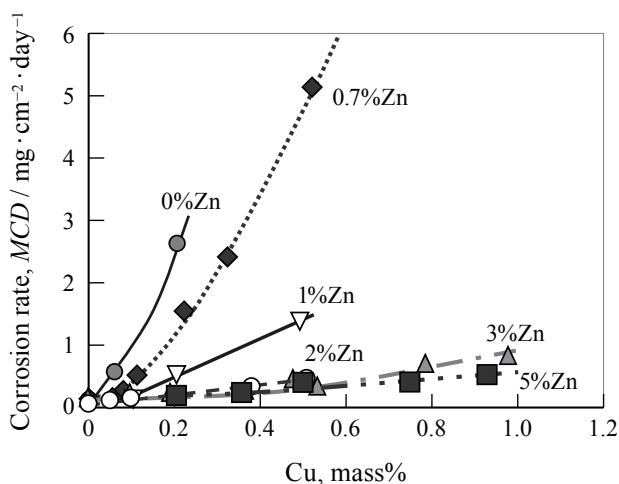
**Figure 2** shows the dependence of the corrosion rate on the Zn content for high-pressure die-cast Mg-9%Al alloys with different amounts of Cu. In the absence of Cu, the corrosion rate is almost independent of the Zn content. It has been reported that the corrosion resistance of pure Mg decreases with increasing zinc content.<sup>(1)</sup> However, this appears not to be the case for the Mg-9%Al alloy in the present study. In contrast, for Cu contents of 0.2% and 0.5%, the corrosion rate is seen to decrease significantly with increasing Zn content up to 2%, and then remains constant. Thus, the addition of 2% or more Zn during the recycling process would be expected to significantly suppress the loss of corrosion resistance due to the presence of Cu.

**Figure 3** shows the corrosion rate for different high-pressure and gravity die-cast Mg-9%Al alloys. It can be seen that the addition of Zn reduces the corrosion rate not only for high-pressure die casting

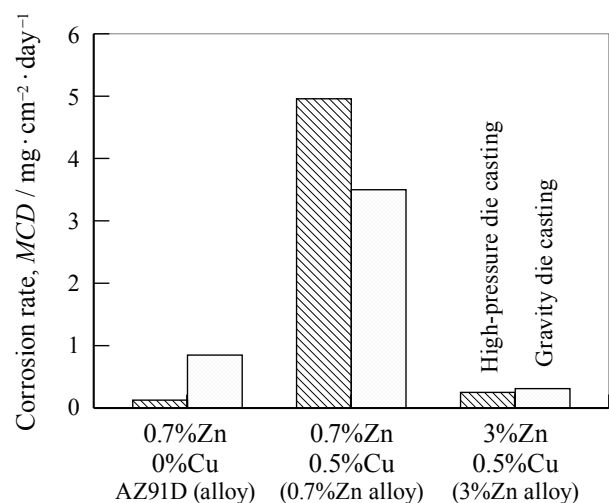
but also for gravity casting in which the cooling rate is relatively small. This means that Zn has the same beneficial effect regardless of the grain size. In the remainder of this paper, two different AZ91 based alloys produced by high-pressure die casting with 0.5% Cu are considered. The first contains 0.7% Zn and, for convenience, is simply referred to as the 0.7%Zn alloy. The second contains 3% Zn and is referred to as the 3%Zn alloy.



**Fig. 2** Relationship between amount of Zn and corrosion rate for high-pressure die cast Mg-9%Al-(0-6)%Zn-(0, 0.2, 0.5)%Cu-0.3%Mn alloys.



**Fig. 1** Relationship between amount of Cu and corrosion rate for high-pressure die cast Mg-9%Al-(0-5)%Zn-(0-1)%Cu-0.3%Mn alloys.

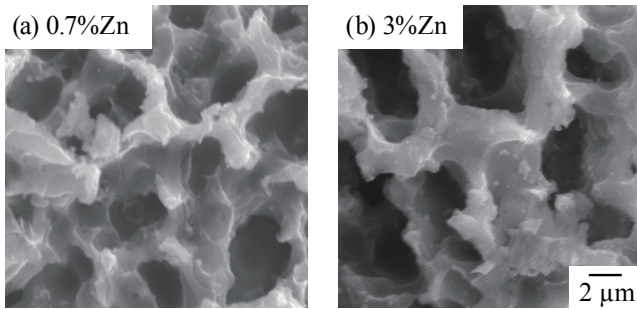


**Fig. 3** Corrosion rate for high-pressure die cast and gravity die cast Mg-9%Al-(0.7, 3)%Zn-(0, 0.5)%Cu-0.3%Mn alloys.

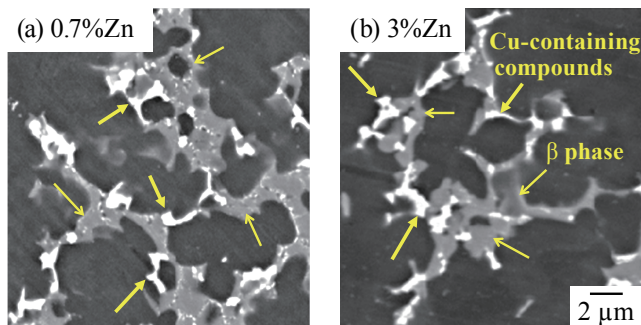
**Figure 4** shows the surface morphology of the 0.7%Zn and 3%Zn alloys following corrosion testing. Both samples appear porous with globular cavities, although the matrix regions are larger in the 3%Zn alloy. Generally speaking, in AZ91D alloys, corrosion begins at the center of  $\alpha$ -Mg regions, and the remaining material consists of the  $\beta$  phase and immediately adjacent  $\alpha$ -Mg regions.<sup>(8,9)</sup> Because the corrosion rate increases with increasing Cu content as shown in Fig. 1, Cu-containing compounds are cathodic. It is considered that the matrix regions of the 3%Zn alloy were larger because the corrosion rate was lower.

**Figure 5** shows SEM images of the microstructure of the 0.7%Zn and 3%Zn samples, and **Fig. 6** shows their chemical composition. In addition to  $\alpha$ -Mg (the matrix phase), gray and white regions are observed for both alloys in Fig. 5. As shown in Fig. 6, the gray regions are  $\beta$ -phase  $Mg_{17}Al_{12}$ , and the white regions

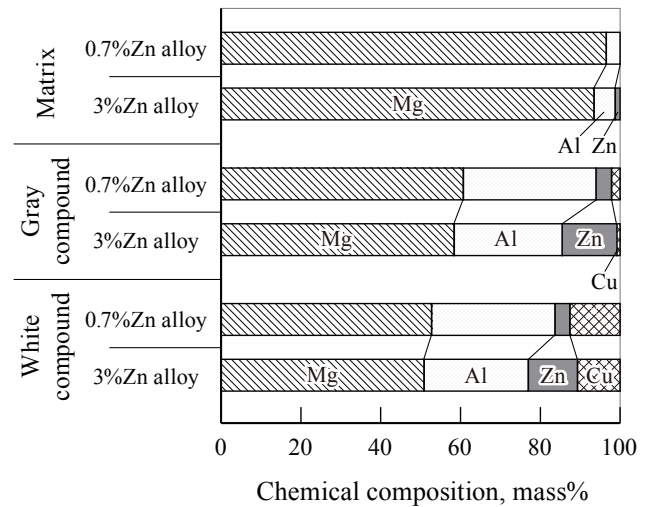
are Cu-containing compounds. With increasing zinc content, the amount of Al and Zn in the  $\alpha$ -Mg increases, the amount of Al in the  $\beta$ -phase decreases slightly, and the amount of Zn in  $\beta$ -phase increases. Also, with increasing Zn content, the amount of Zn in the Cu-containing compounds increases, and the amount of Al and Cu decreases. Thus, it appears that most of the added Zn is present in the  $\beta$ -phase and the Cu-containing compounds.



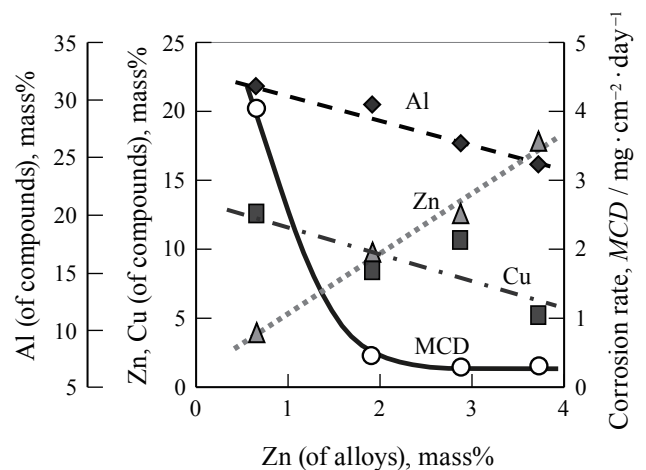
**Fig. 4** Surface morphology after corrosion test:  
(a) Mg-9%Al-0.7%Zn-0.5%Cu-0.3%Mn alloy,  
(b) Mg-9%Al-3%Zn-0.5%Cu-0.3%Mn alloy.



**Fig. 5** Microstructure of high-pressure die cast alloys (BSE image);  
(a) Mg-9%Al-0.7%Zn-0.5%Cu-0.3%Mn alloy,  
(b) Mg-9%Al-3%Zn-0.5%Cu-0.3%Mn alloy.



**Fig. 6** Chemical composition of  $\alpha$ -Mg,  $\beta$  phase and Cu-containing compounds in Mg-9%Al-(0.7,3)%Zn-0.5%Cu-0.3%Mn alloys.



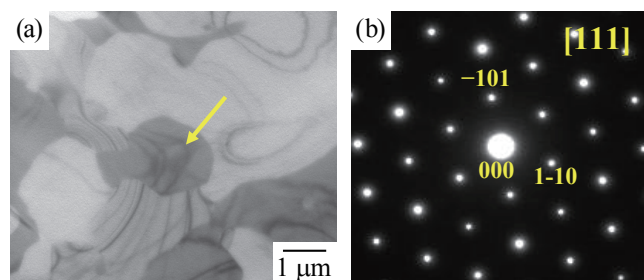
**Fig. 7** Relationship between amount of Zn in high-pressure die cast Mg-9%Al-(0-4)%Zn-0.5%Cu-0.3%Mn alloys and amount of Al, Zn, and Cu in Cu-containing compounds, and alloy corrosion rate.



**Figure 7** shows the effect of the amount of added Zn in Mg-9%Al-(0-4)%Zn-0.5%Cu-0.3%Mn alloys on the Al, Zn, and Cu content of the Cu-containing compounds and the corrosion rate. The Zn content in the compounds increases in proportion to the amount of added Zn, whereas the Al and Cu content decreases. The corrosion rate significantly decreases with increasing Zn content up to 2%, and then remains almost constant. These results suggest that the crystal structure of the Cu-containing compounds change at a Zn content of about 2%.

**Figure 8** shows a TEM image and a selected area diffraction pattern (SADP) of Cu-containing compounds in the 3%Zn alloy. It has been reported that the Cu-containing compound in 0.7%Zn alloy is  $\text{Mg}_6\text{Al}_7\text{Cu}_3$  with a cubic crystal structure and a lattice constant of 1.21 nm.<sup>(9)</sup> However, from the SADP in Fig. 8(b), the compound has a cubic crystal structure with a lattice constant of 1.43 nm and a single phase. From the PDF crystal-structure database, the closest match is  $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$ , which is cubic and has a lattice constant of 1.422 nm. This is consistent with the Mg-Al-Zn ternary phase diagram for Mg-based alloys. When the Zn content is low,  $\alpha$ -Mg and  $\beta$ -phase  $\text{Mg}_{17}\text{Al}_{12}$  are present, whereas for higher Zn content,  $\alpha$ -Mg,  $\beta$ -phase  $\text{Mg}_{17}\text{Al}_{12}$  and  $\text{Mg}_{32}(\text{Al}, \text{Zn})_{49}$  are present. Therefore, we define the Cu-containing compound in 3%Zn alloy as  $\text{Mg}_{32}(\text{Al}, \text{Zn}, \text{Cu})_{49}$ .

It is therefore considered that  $\text{Mg}_6\text{Al}_7\text{Cu}_3$  is initially formed in Mg-9%Al alloy as the Cu content increases, and this leads to a deterioration of the corrosion resistance. However, with increasing Zn content, the  $\text{Mg}_6\text{Al}_7\text{Cu}_3$  changes to  $\text{Mg}_{32}(\text{Al}, \text{Zn}, \text{Cu})_{49}$ , and the corrosion resistance is significantly enhanced.

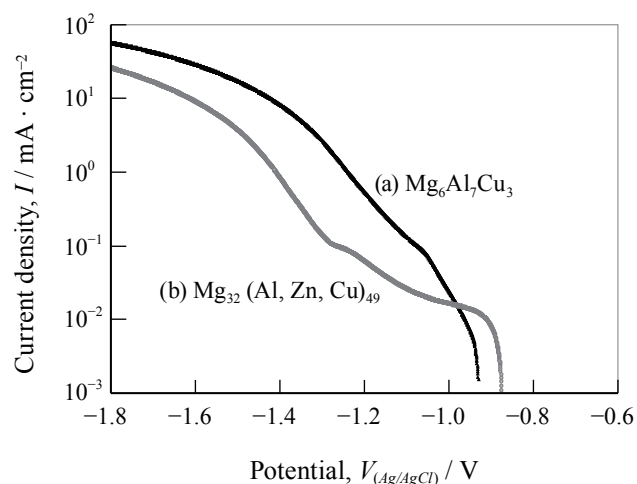


**Fig. 8** TEM images of Cu-containing compounds in Mg-9%Al-3%Zn-0.5%Cu-0.3%Mn alloy: (a) bright-field image, (b) SADP from region indicated by arrow.

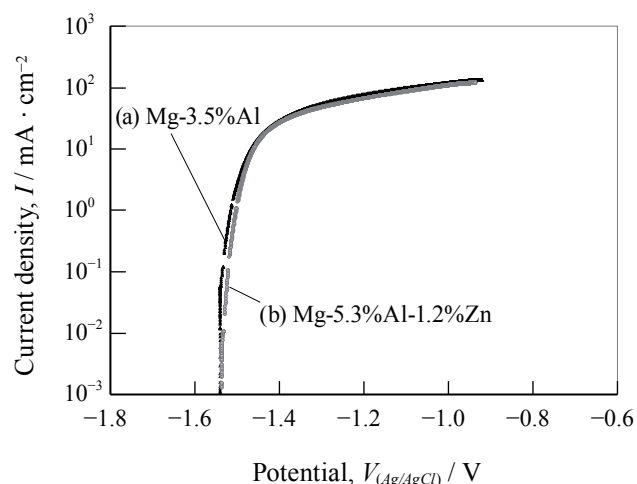
### 3.2 Electrochemical Properties

**Figure 9** shows cathodic polarization curves for Cu-containing compounds in 0.7%Zn and 3%Zn alloy. The potential for  $\text{Mg}_6\text{Al}_7\text{Cu}_3$  is  $-0.92$  V and the current density increases as the electrical potential becomes less noble. On the other hand, the potential for  $\text{Mg}_{32}(\text{Al}, \text{Zn}, \text{Cu})_{49}$  is  $-0.87$  V and is slightly more noble than that for  $\text{Mg}_6\text{Al}_7\text{Cu}_3$ . The current density for both  $\text{Mg}_6\text{Al}_7\text{Cu}_3$  and  $\text{Mg}_{32}(\text{Al}, \text{Zn}, \text{Cu})_{49}$  increases as the electrical potential becomes less noble. However, the rate of increase for  $\text{Mg}_{32}(\text{Al}, \text{Zn}, \text{Cu})_{49}$  is lower.

**Figure 10** shows anodic polarization curves for



**Fig. 9** Cathodic polarization curves for Cu-containing compounds in 5% NaCl solution.



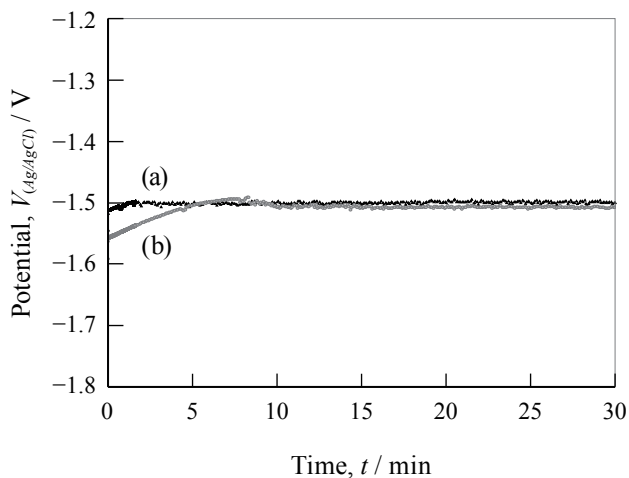
**Fig. 10** Anodic polarization curves for  $\alpha$ -Mg in 5% NaCl solution.

$\alpha$ -Mg in the 0.7%Zn and 3%Zn alloys. The  $\alpha$ -Mg composition in the 0.7%Zn alloy was Mg-3.5%Al, and that in the 3%Zn alloy was Mg-5.3%Al-1.2%Zn. The potential for both alloys is  $-1.54$  V, and their anodic polarization curves are also very similar.

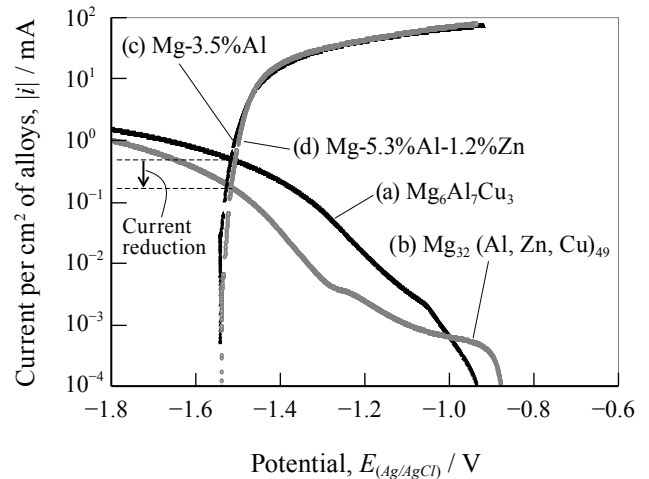
**Figure 11** shows the change in the potential for 0.7%Zn and 3%Zn alloy with time. The final values are seen to be very similar at about  $-1.5$  V.

In order to discuss the corrosion rate for alloys, it is necessary to consider the relative area of the cathodic and anodic regions. Based on microstructural observations, the relative area of the Cu-containing compounds in the 0.7%Zn and 3%Zn alloys was 2.6% and 3.8%, respectively, and the relative area of  $\alpha$ -Mg was 53.1% and 62.8%, respectively. This allowed the current densities in Figs. 9 and 10 to be converted into electrical current values in a 1-cm<sup>2</sup> region of the alloy samples, and the results are shown in **Fig. 12**. The potential at the intersection point between the cathodic curve (Fig. 12(a)) and the anodic curve (Fig. 12(c)) for the 0.7%Zn alloy, and that between the cathodic curve (Fig. 12(b)) and the anodic curve (Fig. 12(d)) for the 3%Zn alloy is almost the same (about  $-1.5$  V), which is also the potential for the two alloys (Fig. 11). However, the current at the intersection point is lower for the 3%Zn alloy. Therefore, the 0.7%Zn alloy corrodes faster than the 3%Zn alloy although the potential is almost the same for both.

It can therefore be concluded that the main factor leading to improvement of the corrosion resistance by



**Fig. 11** Potential in 5% NaCl solution:  
(a) Mg-9%Al-0.7%Zn-0.5%Cu-0.3%Mn alloy,  
(b) Mg-9%Al-3%Zn-0.5%Cu-0.3%Mn alloy.



**Fig. 12** Comparison between cathodic polarization curves for (a) Mg<sub>6</sub>Al<sub>7</sub>Cu<sub>3</sub> and (b) Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub>, and anodic polarization curves for (c) Mg-3.5 mass%Al and (d) Mg-5.3 mass%Al-1.2 mass%Zn per cm<sup>2</sup> of alloy in 5% NaCl solution.

adding Zn to AZ91 alloy containing Cu was a decrease in the cathodic current density in the Cu-containing compounds. This occurred because Mg<sub>6</sub>Al<sub>7</sub>Cu<sub>3</sub> changed to Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub> with increasing Zn content in the alloy, the cathodic reaction rate significantly decreased, the anodic reaction rate decreased to balance this, and the corrosion rate was reduced.

#### 4. Summary

The corrosion resistance, microstructure, and electrochemical properties of Mg-9%Al-(0-6)%Zn-(0-1)%Cu-0.3%Mn alloys, which were AZ91 alloys with different Zn and Cu contents, were investigated. The results obtained are summarized as follows:

- (1) The corrosion resistance of Mg-9%Al alloy decreased with increasing Cu content but was significantly improved with increasing Zn content, particularly 3% Zn or higher.
- (2) During corrosion testing of 0.7%Zn and 3%Zn alloys, it was found that corrosion occurred in the center of  $\alpha$ -Mg regions, and the remaining material was the  $\beta$  phase with adjacent  $\alpha$ -Mg regions, together with Cu-containing compounds. It was considered that the cathodic compound in the 0.7%Zn alloy was Mg<sub>6</sub>Al<sub>7</sub>Cu<sub>3</sub>, whereas that in the 3%Zn alloy was Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub>.
- (3) By adding Zn to AZ91 alloy containing Cu,

Mg<sub>6</sub>Al<sub>7</sub>Cu<sub>3</sub> with a large cathodic current changed to Mg<sub>32</sub>(Al, Zn, Cu)<sub>49</sub> with a small cathodic current, and the corrosion resistance was significantly enhanced.

### References

- (1) Hanawalt, J. D., Nelson, C. E. and Peloubet, J. A., *Trans. Am. Inst. Mining Metall. Eng.*, Vol. 147 (1942), pp. 273-299.
- (2) Hillis, J. E., *SAE Tech. Pap. Ser.*, No. 830523 (1983).
- (3) ASTM Standard, B-94.
- (4) Emley, E. F., *Principles of Magnesium Technology* (1966), pp. 180-183, Paragon Press.
- (5) Kojima, Y., *J. Jpn. Inst. Light Metals*, Vol. 58, No. 10 (2008), pp. 526-548.
- (6) Blawert, C., Morales, E., Dietzel, W., Kainer, K. U., Scharf, C. and Ditze, A., *SAE Tech. Pap. Ser.*, No. 2006-01-0254 (2006).
- (7) The Japan Magnesium Association, *Handbook of Advanced Magnesium Technology* (2000), p. 311, Kallos publishing.
- (8) Lunder, O., Lein, J. E., Aune, T. Kr., and Nisancioglu, K., *Corrosion*, Vol. 45, No. 9 (1989), pp. 741-748.
- (9) Aune, T. Kr., Lunder, O. and Nisancioglu, K., *Microstructural Science*, Vol. 17 (1989), pp. 231-241.

Figs. 1 and 4

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Figs. 1-2, 4-5 and 7

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Figs. 4-5, 8-12 and Table 2

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