Effects of Microstructure on Discharge Behavior of AZ91 Alloy as Anode for Mg–Air Battery

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The effects of precipitate distribution in commercial Mg alloys on the discharge behavior of a Mg–air battery were investigated. Rolled Mg–9 mass%Al–1 mass%Zn (AZ91) alloy sheets were selected as the anode. The discharge behaviors were evaluated by constant current discharge tests, and the corrosion behaviors were estimated by salt immersion tests and potentiodynamic polarization measurements. In the discharge tests, the peak-aged specimens exhibited much shorter discharge time than the solution-treated specimen. In the corrosion tests, the aged specimens exhibited quite a low corrosion rate as compared with the solution-treated specimen. From the potentiodynamic polarization measurements, the aged specimens showed a much lower corrosion current density and higher corrosion potential than the solution-treated specimen. It is suggested that a stable corrosion barrier by densely distributed β-phase precipitates contributed to both the reduction of discharge time and the suppression of corrosion rate for the aged specimens. Microstructural evaluations of the aged specimens revealed that fine β-phase precipitates were densely distributed throughout the specimens and that there was little Al-rich α phase, which would accelerate galvanic corrosion between the α matrix and the β phase. It was confirmed that the finely and homogenously distributed β phase in the aged AZ91 specimens acted as a barrier to the dissolution of the α-Mg matrix because a large Al-rich α phase was not distributed in the AZ91 specimens in this study. [doi:10.2320/matertrans.MC201403]

(Received February 4, 2014; Accepted March 12, 2014; Published July 25, 2014)

Keywords: magnesium alloys, magnesium-air battery, corrosion, microstructure, heat treatment

1. Introduction

Mg alloys are promising light structural materials because of their low density, high specific strength and stiffness, and they are widely used in the automobile and consumer electronics industries.¹) Recently, Mg alloys have also attracted attention as anodes in Mg–air batteries, which are a promising power source and energy storage device owing to their high theoretical voltage, high current capacity, and environmental friendliness.²) However, Mg–air batteries are not as well known as Al– and Zn–air batteries because of the less attractive properties of Mg anodes. It is reported that effective methods for improving the properties of Mg anodes include suppressing oxide film formation on the anode surface and suppressing the excessive dissolution of the anodes during discharge.³–⁶) It is suggested that the composition of the Mg alloy anodes is one of the key parameters for improving their properties. For example, Ma et al.⁵) reported that Mg–Li–Al–Ce alloys exhibited higher anode performance than commercial Mg alloys (pure Mg and AZ31) because discharge products on the anode surface became loose, which retained a large reaction surface during charge. Zhao et al.⁷) reported the superior discharge behavior of Mg–Ga–Hg alloy anodes as compared with anodes of commercial Mg alloys because the addition of Ga accelerates stripping of the corrosion film and the formation of Mg amalgams, thus promoting electrochemical activity.

Meanwhile, differences in microstructure such as precipitate distribution, are known to be important factors for controlling the corrosion behavior of Mg alloys.⁸–¹⁰) Concerning commercial Mg alloys (Mg–Al series alloys), the (Mg₁₇Al₁₂) phase provides a shield against corrosion of the α phase by forming a continuous network around the grain boundaries.¹¹–¹⁸) On the other hand, the β phase occasionally acts as a cathode when it precipitates discontinuously in and around grain boundaries.¹⁹–²⁰) These reports indicate that a microstructural factor may play an important role in the discharge behavior of Mg alloy anodes; however, the relationship between the microstructure of Mg alloys and their discharge behavior as an anode is still unclear.

In the present study, the effects of precipitate distribution in commercial Mg alloys on the discharge behavior of a Mg–air battery were investigated and the relationships between the microstructure, discharge behavior, and corrosion behavior of the commercial Mg alloys as anodes are discussed.

2. Experimental

AZ91 alloy sheets were selected as the Mg–air battery anode in this study because precipitation (β phase) distribution is easily controlled by aging. The AZ91 alloy sheets were prepared by the following procedure. An AZ91 alloy bar 60 mm in length, 50 mm in width, and 5 mm in thickness was extruded from a commercial AZ91 ingot. The composition of the AZ91 alloy in this work is shown in Table 1. The extruded bar was heated at 703 K and then unidirectionally rolled at a rolling reduction of 20%. The heating and rolling treatments were repeated until the alloy reached a thickness of 1 mm. The rolled specimens were then solution heat treated at 698 K for 24 h. After that, aging was carried out at 473 K for 10, 16, 19, and 24 h.

The discharge performance of the Mg–air battery was investigated by constant current discharge tests at a current...
density of 10 mA·cm⁻² at room temperature. Voltage versus time was recorded up to a cutoff voltage of 0.5 V. The anodic efficiency and discharge capacity were calculated using eqs. (1) and (2), respectively:

\[
\text{Anodic efficiency (\%) = } \frac{i \times A \times t \times M_a}{2F(W_i - W_f)} \times 100\% \quad (1)
\]

\[
\text{Discharge capacity (mAh/g) = } \frac{i \times A \times t}{W_i - W_f} \quad (2)
\]

where \(i\) is the current density (mA·cm⁻²), \(t\) is the discharge time (h) of the discharge test, \(F\) is the Faraday constant (96485 C·mol⁻¹), \(A\) is the surface area (cm²), \(M_a\) is the atomic mass (g·mol⁻¹) of the specimens, and \(W_i\) and \(W_f\) are the weight of the specimens before and after the discharge test, respectively.⁵)

The AZ91 specimens with dimensions of 25 mm × 35 mm × 1 mm, an activated carbon sheet electrode (supplied by the NIPPON VALQUA INDUSTRIES, LTD), and a 5 mass% NaCl aqueous solution were used as the anode, cathode, and electrolyte, respectively, of the Mg-air battery. The surfaces of the anode specimens were preliminary polished with #1000-grit SiC abrasive paper.

For corrosion testing, AZ91 specimens prepared in the same manner as the anode specimens were used. Salt immersion tests were then performed for 72 h in a 5 mass% NaCl solution saturated with Mg(OH)₂ (pH 10.0) using a Princeton applied research VersaSTAT3 electrochemical measurement system. The reference electrode was a saturated calomel electrode (SCE). Potentiodynamic polarization curves were measured with respect to the open-circuit potential at a scanning rate of 1 mV/s from −200 to 350 mV.

The microstructures of the anode specimens were observed by optical microscopy (OM) and transmission electron microscopy (TEM). Phase identification of the anode specimens was performed by energy dispersive X-ray spectroscopy (EDS) and X-ray diffractometry (XRD). The Vickers hardness was measured at ten randomly selected points for each sample using a load of 0.98 N for 10 s.

### 3. Results and Discussion

Figure 1 shows the microstructures of the solution-treated specimen and the 10, 16, 19, and 24 h-aged specimens. The average grain size of the solution-treated specimen and the 10, 16, 19, and 24 h-aged specimens was 102, 106, 96, 99, and 100 µm, respectively, indicating that the grain size was not affected by the aging. The microstructure of the solution-treated specimen was composed of only a single phase (α-Mg matrix). In the case of the aged specimens, not only an α-phase region (white) but also a black region was found near the grain boundaries. Figure 2 shows the XRD patterns of all the specimens in Fig. 1. In the aged specimens, a β-Mg₁₇Al₁₂ phase was detected, in addition to the α phase, implying that the black region in Fig. 1 corresponds to the β phase. It should be noted that the peak intensity of the β phase had a maximum value in the 19 h-aged specimen.

The age-hardening response of the AZ91 specimens at 473 K is illustrated in Fig. 3. The hardness increment of the specimens was approximately 20 HV, and the peak hardness was observed at 19 h. The aging time for peak hardness corresponded to the results of the XRD measurement, where the peak intensity of the β phase had a maximum value at 19 h.
The discharge behaviors of the Mg-air battery are shown in Fig. 4 and Table 2. Figure 4 shows the voltage–time curves of the Mg-air battery, in which the solution-treated (ST) and aged specimens were applied as anodes, and Table 2 is the summary of the measured values (discharge time, operating voltage, anodic efficiency, and discharge capacity) from the voltage–time curves. In the solution-treated specimen, a constant voltage of 1.1 V continued up to 3 h and then decreased gradually. The final discharge time was 6.56 h. However, the voltage rapidly decreased in all the aged specimens as compared with the solution-treated specimen, and the 19 h-aged specimen exhibited the shortest discharge time among the aged specimens. The 24 h-aged (over-aged) specimen had a slightly higher discharge time than the 19 h-aged specimen. It seems that precipitation of the fine metastable phase created by the aging process has a detrimental effect on the discharge time of the Mg-air battery. Large differences were not observed in the other measured values (operating voltage, anodic efficiency, and discharge capacity) of the solution-treated and aged specimens. Thus, it is clear that the aging treatment of the AZ91 specimen affects the discharge time of the Mg-air battery; however, it does not exert an influence on the other discharge properties.

Next, the corrosion and electrochemical properties of the AZ91 specimens were evaluated. The self-corrosion rate obtained by weight loss measurements is shown in Fig. 5. The corrosion rate of the solution-treated (ST) and aged AZ91 specimens was approximately 7 times higher than those of the aged specimens. One researcher reported that a higher corrosion rate was obtained in a T6-treated cast AZ91 alloy compared with a solution-treated cast AZ91 alloy. On the other hand, other researchers reported that the T6-treated AZ91 cast alloy exhibited a lower corrosion rate than the solution-treated AZ91 cast alloy because finely and

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**Table 2 Discharge performance of Mg-air battery with solution-treated (ST) and aged AZ91 specimens.**

<table>
<thead>
<tr>
<th>Heat treatment</th>
<th>Discharge time (h)</th>
<th>Operating voltage (V)</th>
<th>Anodic efficiency (%)</th>
<th>Discharge capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ST</td>
<td>6.56</td>
<td>0.95</td>
<td>54.6</td>
<td>1204</td>
</tr>
<tr>
<td>10 h-aging</td>
<td>5.31</td>
<td>0.74</td>
<td>56.4</td>
<td>1244</td>
</tr>
<tr>
<td>16 h-aging</td>
<td>1.15</td>
<td>0.91</td>
<td>55.2</td>
<td>1218</td>
</tr>
<tr>
<td>19 h-aging</td>
<td>0.66</td>
<td>0.82</td>
<td>52.9</td>
<td>1167</td>
</tr>
<tr>
<td>24 h-aging</td>
<td>3.48</td>
<td>0.80</td>
<td>55.7</td>
<td>1229</td>
</tr>
</tbody>
</table>

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homogenously distributed \(\beta\) phases act as a barrier against the development of corrosion of the \(\alpha\) phase. The current experimental results seem to demonstrate a tendency toward the latter results. It is considered that the low corrosion rate of the aged specimens in Fig. 5 is directly correlated with the small discharge time of the Mg-air cell with the aged specimens as the anode, as shown in Fig. 4.

Figure 6 shows the potentiodynamic polarization curves of the solution-treated and aged specimens, and the corrosion parameters calculated by Tafel linear extrapolation are summarized in Table 3. Explicit differences in the curves were found between the solution-treated and aged specimens, and these results were well consistent with those of the self-corrosion rate measurements. The aged specimens exhibited much lower corrosion current density than did the solution-treated specimen, and the 16 and 19 h-aged specimens showed higher corrosion potential, which implies reduced electrochemical activity.\(^4,7\) The sudden drop in the anodic current density observed in the 10 and 24 h-aged specimens results from local pitting of Mg and its alloys.\(^8\) Evidence of local pitting confirms the destruction of oxide films or corrosion products formed on the specimen surface. On the other hand, in the 16 and 19 h-aged specimens, a sudden drop in anodic current was not observed, indicating that dissolution of the \(\alpha\) phase was difficult to accomplish, even when an overpotential was applied. The polarization curves indicate that a stable corrosion barrier was formed by densely distributed \(\beta\)-phase precipitates in the peak-aged specimen, which caused both the reduction of discharge time and the suppression of the corrosion rate.

Next, the reasons why the \(\beta\) phase did not act as an anode against the \(\alpha\) phase and instead behaved as a corrosion barrier are as follows. Figure 7 shows the transmission electron micrographs of the 16 h-aged specimen. As shown in Fig. 1, the microstructures of the aged specimens were composed of a black region, where \(\beta\)-phase precipitates were densely distributed, and a white \(\alpha\)-phase region, where \(\beta\) phase precipitates were not observed, at least at the magnification of OM. On the other hand, fine, needle-like \(\beta\) precipitates approximately 20 nm in width and a few hundred nanometers in length were observed in the \(\alpha\)-phase region in Fig. 7. In the black region, the \(\beta\) phase precipitates as larger elliptical precipitations than those in white region were densely distributed. Figure 7 suggests that fine \(\beta\)-phase precipitates were densely distributed throughout the aged specimens. The high-magnification micrograph of the \(\beta\)-phase precipitates and the results of the elemental analyses by EDS are summarized in Fig. 8. The EDS results indicate the 16 h-aged specimen had only a high concentration gradient with about 20 nm at the precipitation boundaries. Hakamada et al.\(^{23}\)
behaviors may vary with the process conditions during casting. As described above, the large area of the Al-rich α phase was not detected in the aged AZ91 specimens in this study because of the sheet making processes. Therefore, it is conclusively demonstrated that the finely and homogeneously distributed β phase in the aged AZ91 specimens acts as a barrier to the dissolution of the α-Mg matrix because the large area of Al-rich α phase was not distributed in the AZ91 specimens in this study.

It is interesting to note that the other discharge properties such as operating voltage, anodic efficiency, and discharge capacity of the aged AZ91 specimens had almost the same values as the solution-treated specimens, as shown in Table 2. Ma et al. reported the superior discharge properties (anode efficiency and discharge capacity) of the Mg–Li–Al–Ce alloy anode of a Mg–air battery, and suggested that its superior discharge properties can be attributed to the modification of discharge products on the anode surface by alloying. The discharge products of the Mg–Li–Al–Ce alloy become looser than those of AZ series alloys. These loose discharge products promote many pores and cracks on the surface film and contribute to the creation of a large reaction surface during discharge, resulting in superior anode efficiency and discharge capacity. A series of experiments in this study and the results of a previous report indicate that the shape and distribution of β-phase precipitates in the anode specimen likely do not affect the anode efficiency and discharge capacity; however, the composition of the primary α phase likely plays a significant role in the discharge properties of Mg–air batteries. Investigations clarifying the effects of alloy composition (aluminum and zinc concentrations) on the discharge properties are still in progress.

4. Conclusions

The effects of precipitate distribution in AZ91 Mg alloys on the discharge behavior of a Mg–air battery were investigated and the relationships between microstructure (precipitate distribution), discharge behavior, and corrosion behavior were evaluated. The results are concluded as follows:

1. In the discharge tests, the peak-aged specimens exhibited much shorter discharge time than the solution-treated specimen, whereas the other discharge properties such as operating voltage, anodic efficiency, and discharge capacity of the aged specimens had almost the same values as the solution-treated specimen.

2. In the corrosion tests, the aged specimens exhibited a very low corrosion rate as compared to the solution-treated specimen. From the measurements of potentiodynamic polarization curves, the aged specimens showed a much lower corrosion current density and higher corrosion potential than the solution-treated specimen. Also, evidence of local pitting, which indicates dissolution of the α phase, was not observed in the peak-aged specimens. It is suggested that a stable corrosion barrier of densely distributed β-phase precipitates was formed in the peak-aged specimen and that the corrosion barrier resulted in both the reduction of discharge time and the suppression of corrosion rate.

<table>
<thead>
<tr>
<th>Mg (at%)</th>
<th>Al (at%)</th>
<th>Zn (at%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 65.9</td>
<td>29.1</td>
<td>5.0</td>
</tr>
<tr>
<td>2 87.6</td>
<td>10.4</td>
<td>1.9</td>
</tr>
<tr>
<td>3 93.1</td>
<td>5.4</td>
<td>1.5</td>
</tr>
<tr>
<td>4 93.3</td>
<td>4.9</td>
<td>1.7</td>
</tr>
</tbody>
</table>

Fig. 8 The magnified EDS image around the β phase [shown as needle-like precipitates in Fig. 7(a)], in which the chemical compositions at the interface between the β and α-phases are listed.
TEM observation and EDS analysis of the aged AZ91 specimen revealed that fine β-phase precipitates were densely distributed throughout the specimens and that there was little segregation of Al and Zn solutes around the β-phase precipitates, which accelerated galvanic corrosion between the α and β phases. Therefore, it is confirmed that the finely and homogenously distributed β phase in the aged AZ91 specimens acted as barrier to the dissolution of the α-Mg matrix because a large area of Al-rich α phase was not distributed in the AZ91 specimens in this study.

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