Evaluation of Pitting Corrosion Mechanism of AZ31 Magnesium Alloy by Monitoring Acoustic Emission

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The aim of this study was to evaluate the electrochemical corrosion mechanism of AZ31 magnesium alloy by monitoring acoustic emission (AE). AE signals were monitored in situ during the potentiodynamic corrosion test. Evolution of AE signal appeared to be divided into four distinct stages (AE stage I, II, III, and IV) according to the corrosion time and mechanism. AE characteristics in each AE stage were correlated with the bubble behavior, reflecting corrosion mechanism. This interpretation was verified with the simultaneous observation of corrosion bubbling by video camera.

Keywords: corrosion mechanism, magnesium alloy, acoustic emission, bubbling behavior

1. Introduction

Magnesium alloys have been candidates for light structural components because of their good specific strength. In spite of this advantage, their poor corrosion resistance due to high electrochemical activity is an obstacle to their widespread use.

Corrosion mechanism is usually studied by several analytical methods such as electrochemical polarization, electrochemical impedance spectroscopy, and the identification of corrosion products.\(^1,2\) For in situ investigation of the corrosion mechanism, acoustic emission (AE) technique has been applied particularly for steel.\(^3–6\) This is a non-destructive evaluation technique for analyzing the transient elastic wave generated by the rapid release of internal energy in the material. The AE generation during corrosion of metals, particularly steel, is mainly attributed to gas bubbling.\(^3–6\) Fracture of pit cover and passive film breakage may possibly produce AE signal during the corrosion of steel.\(^6\) Although the use of AE technique for corrosion study has been reported, the detailed evolution of the AE signal has not been experimentally validated by matching with in situ observations. Moreover, only very few AE investigations on the corrosion of magnesium alloy are available.\(^7\)

In the present study, corrosion mechanism at the specific stages of electrochemical polarization of the AZ31 magnesium alloy was correlated with the corresponding AE behavior. This interpretation was verified by in situ video monitoring of the bubbling behavior on the surface of the specimen.

2. Experimental Procedure

A commercial rolled AZ31 alloy (2.5–3.5 mass% Al, 0.6–1.4 mass% Zn, 0.2–1.0 mass% Mn, 0.1 mass% Si, Fe < 0.005 mass%, Cu < 0.04 mass%, and Ni < 0.005 mass%) was used for this investigation. A three electrode configuration consisting of a vertically positioned working electrode (i.e. specimen), a reference Ag/AgCl electrode, and a Pt counter electrode was set-up for cathodic and anodic polarization test. A salt bridge was utilized to remove the effect of H₂ gas bubbling on the counter electrode during corrosion by placing the counter electrode in a separated nearby corrosion test cell. The corrosion test was performed in a 3.5 mass% NaCl solution at pH 7. The specimen was polarized positively by an open circuit potential with a scan rate of 0.4 mV/s. An AE sensor (Model: R15, Physical Acoustics Co., Princeton, USA) of a nominal resonant frequency of 150 kHz was employed. The AE signals were collected in an acquisition device (Model: PCI 2, Physical Acoustics Co., Princeton, USA). The threshold value was set as 27 dB, and the pre-amplifier was set at 40 dB, respectively. Details on the experimental set-up are available in our previous reports.\(^4,6\) Real-time images were simultaneously recorded on video during pitting corrosion for correlating the AE signals with corrosion characteristics.

3. Results and Discussions

Figure 1 shows the potentiodynamic polarization curve of the AZ31 alloy in match with the evolution of AE cumulative counts. This alloy shows a typical polarization behavior with a cathodic and anodic reaction. The cumulative AE counts increased with corrosion time, and the corrosion process ap-
pears to be divided into four distinct stages. Figures 2–6 shows a series of video images at a specific instant in each stage of pitting corrosion and the corresponding schematic illustration of the bubbling behavior observed, respectively.

In stage I, the electrochemical cathodic reaction occurred resulting in decreased current density with voltage. In this period, H₂ gas bubbles were formed according to the following cathode reaction in the neutral solution:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \] (1)

The formation and expansion of gas bubbles was easily observed on the surface of the working electrode (i.e., specimen) as shown in Fig. 2. The H₂ bubbles ascended along the surface of the vertically positioned specimen. A large number of bubbles gathered and burst on the surface of the solution, resulting in AE signal generation. Depending on the decrease in the current density with voltage in stage I, the generation rate of cathodic bubbles gradually decreased. Hence, the cumulative of AE counts initially increased rapidly and then gradually towards the end of stage I.

In stage II, after a specific corrosion potential (i.e., −1.49 V), the current density increased abruptly towards a steady value. From the corrosion potential, an anodic reaction starts to occur on the specimen according to eq. (2). Right following this instant reaction, magnesium hydroxide (Mg(OH)₂), acting as a weak passivation film, forms according to eq. (3). Because of this passivation film, pitting corrosion did not appear despite the anodic reaction in stage II.

\[ \text{Mg} \rightarrow \text{Mg}^{2+} + 2e^- \] (2)

\[ \text{Mg}^{2+} + 2(\text{OH})^- \rightarrow \text{Mg(OH)}_2 \] (3)

During this time, only a few big bubbles that were generated, but not broken-up, were still attached on the specimen, as shown in Fig. 3. There was almost no AE signal in stage II; hence, there was no increase in the cumulative AE counts, indicating that no gas bubbles and no other detectable AE sources were involved.

Stage III is a period that the current density increases because of the initial pitting process, resulting in formation of small pits on the specimen as shown in Fig. 4. In this stage, there was no significant increase in the AE cumulative counts, even though small pits start to occur. This implies that there is a time delay before the first detection of an active AE signal. The time delay for AE detection of corrosion can be attributed to the threshold amount of bubbles required for AE sensing which may imply that the longer the period, the higher the pitting resistance of that metal.

Stage IV is a severe pitting corrosion period (i.e., increase in current density) accompanying a corresponding increase in the AE cumulative counts. In this stage, severe anodic dissolution reaction of the metal (i.e., corrosion) occurred. This corrosion process generates H₂ bubbles largely by the following hydrolysis reaction (i.e., eq. (4)) and the subsequent reduction of H⁺ ions to hydrogen molecules (i.e., eq. (5)):

\[ \text{Mg}^{2+} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}^- + \text{H}^+ \] (4)

\[ 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \] (5)

The observed large increase in the cumulative AE counts was attributed to hydrogen bubbles generated because of the above hydrolysis reaction. The H₂ bubbles formed by the hydrolysis appear to be a dense succession of bubbling flow as shown in Fig. 5. Large area of the specimen was corroded at the end of stage IV as shown in Fig. 6.

Figure 7 shows the duration of each AE signal (i.e., AE hit) detected during the electrochemical corrosion test and a typi-
cal time-domain signal in stages I and IV, respectively. AE signals of short duration (< 400 μs) were dominant in stage I, whereas those of longer duration (< 800 μs) were dominant in stage IV. Although the source of AE signals was the hydrogen bubbles in both cases, their bubbling behavior is different. In stage I, a large number of isolated bubbles formed by a cathodic reaction result in a “burst-like” pulse waveform as presented in Fig. 8(a). Corrosion bubbles generated by the hydrolysis reaction in stage IV show a “cloud-like” bubble type as observed in Fig. 5 (i.e., succession of a large number of small bubbles), resulting in a more continuous AE waveform of longer duration as presented in Fig. 8(b).

In summary, corrosion characteristics and corresponding video and AE observations at each stage are given in Table 1. The AE signals of hydrogen bubbles were detected and divided into four stages according to the corrosion mechanism. By analyzing the signals, the amount of hydrolysis bubbles and bubble-type, which reflects the degree of pitting corrosion and corrosion mechanism can be investigated in situ.

4. Conclusion

According to the corrosion mechanism, the AE signals detected during the electrochemical corrosion of AZ31 magnesium alloy were divided into four distinct stages. The generation of AE signals was attributed to the isolated hydrogen bubbles produced by the cathodic reaction and a series of hydrogen bubbles produced by hydrolysis during pitting cor-

![Image](image_url)

**Fig. 6**  In situ video image at the end of stage IV and a corresponding schematic of the observed bubbling behavior.

![Image](image_url)

**Fig. 7**  Duration of each AE signals detected during electrochemical corrosion process of the AZ31 alloy.

![Image](image_url)

**Fig. 8**  A typical AE waveform at different stage generating hydrogen bubbles: (a) stage I and (b) stage IV.

<table>
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<tr>
<th>Table 1</th>
<th>Summary of corrosion characteristics and corresponding video and AE observations at each stage.</th>
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<tbody>
<tr>
<td>Stage</td>
<td>Corrosion time (s)</td>
</tr>
<tr>
<td>I</td>
<td>$0 &lt; t &lt; 1373$ (1373)</td>
</tr>
<tr>
<td>II</td>
<td>$1374 &lt; t &lt; 1637$ (263)</td>
</tr>
<tr>
<td>III</td>
<td>$1638 &lt; t &lt; 1688$ (50)</td>
</tr>
<tr>
<td>IV</td>
<td>$t &gt; 1688$</td>
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rosion. No AE signal was generated with the formation of weak passivation film. Based on the verification with video monitoring of the corrosion behavior, the AE signal analysis was proposed as a nondestructive evaluation method for in situ monitoring of the degree of corrosion and corrosion mechanism of AZ31 alloy.

REFERENCES