Investigation of Stress Corrosion Cracking Behaviors of an AZ91 Magnesium Alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ Solution Using Slow Strain Rate Test}

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The stress corrosion cracking (SCC) behavior of an as-cast AZ91 magnesium alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ solution was investigated using slow strain rate test (SSRT). The results showed that both the uncharged and charged AZ91 alloy occurred transgranular stress corrosion cracking (TGSCC), which were characteristic of large-plane cleavage fracture. Pre-charging had little influences on mechanical properties. It indicated that hydrogen embrittlement (HE) was the main mechanism for the SCC of AZ91 alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 solution.}

[doi:10.2320/matertrans.MC200711]

(Received October 10, 2007; Accepted December 13, 2007; Published April 25, 2008)

Keywords: AZ91 magnesium alloy, stress corrosion cracking, slow strain rate test, hydrogen embrittlement

1. Introduction

Magnesium has a standard potential of $\text{E}^{\circ} = -2.37 \text{V/NHE}$ in acid solution and $\text{E}^{\circ} = -2.69 \text{V/NHE}$ in alkaline solution.$^{1,2}$ It indicates that hydrogen generation in the whole pH range is possible. Some hydrogen atoms forming during the corrosion process would diffuse through the semiconductor film, and into the interior of matrix. It might influence the corrosion and stress corrosion cracking behaviors of magnesium and its alloys in aqueous solutions. In the meantime, the atmospheric pollution caused by acidic rain has been paid more attention in recent years, which is a convenient medium for hydrogen generation.

In our previous works,$^{3,4}$ the corrosion behaviors of as-cast AZ91 magnesium alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ solution were investigated using electrochemical methods. It was found that corrosion films forming on surface during the corrosion process changed with the increase of immersion time, which would directly influence the corrosion behaviors of AZ91 alloy and hydrogen transport through the semiconductor films. It had been confirmed by our subsequent work using Mott-Schottky tests.$^{5}$ Moreover, the hydrogen atoms produced by corrosion reaction during immersion or cathodic charging diffused through the semiconductor corrosion films and into the interior of matrix, enriched at $\beta$ phase, reacted and formed magnesium hydride. Owing to the incoherence of hydride and $\beta$ phase, some hydrogen atoms might combine into hydrogen gas at the interfaces of hydride and $\beta$ phase. When the inner stress caused by hydrogen pressure and expansion stress of formation of magnesium hydride was above the fracture strength, magnesium hydride would be brittle fractured.$^{5}$ What is more, the process of crack initiation and propagation on the charged AZ91 alloy was also \textit{in situ} observed using environmental scanning electron microscope (ESEM).$^{6}$ It indicated that hydrogen had great effects on corrosion behavior of AZ91 alloy, and promoted the crack initiation on $\beta$ phase. It might have a negative influence on the SCC behavior. According to Winzer,$^{7}$ the total hydrogen flux would accelerate due to stress and concentration gradients, which would be another factor for the hydrogen invasion. Therefore, the work about the effect of hydrogen on the SCC of AZ91 alloy in sodium sulfate solution was very important.

In present research, the SCC behaviors of AZ91 alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ solution were investigated using SSRRT. Special attention was paid to the effect of hydrogen on the SCC behaviors of AZ91 alloy.}

2. Experimental Procedure

The material used was as-cast AZ91 magnesium alloy. Its chemical composition (mass.%) was 8.89Al, 0.78Zn, 0.21Mn, <0.001Ni, 0.002Fe, 0.002Cu and balance Mg. The sample surface was polished using 1000, 2000 grit silicon carbide papers, cleaned with distilled water and acetone, and dried in cool air. Some mechanically polished samples were galvanostatic charging at 27.8 \text{mA/cm}^2 for 3h in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ solution (pro-analysis grade, pH = 6.1). After cathodic charging, the solution was changed.}

SSRT was used to investigate the SCC behaviors of AZ91 alloy in 0.1 \text{kmol/m}^3 \text{Na}_2\text{SO}_4 \text{ solution (pro-analysis grade, pH = 6.1) in contact with air at about 30° C. The gauge geometry of the plane-plate samples was 25 \times 8 \times 2.5 \text{mm.}

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The strain rate was $1 \times 10^{-6} \text{ s}^{-1}$. The test for each corrosive medium was repeated three times. Assumed that the deformation over the entire gauge section of samples was uniform, the average specimens elongation was measured by two linear variable displacement transducers (LVDs) attached at two sides of samples. Therefore, the actual strain and actual strain rate, caused by mechanical rupture or SCC, could not be measured using this equipment. The procedure was described in detail in our previous work.8)

### 3. Results

#### 3.1 Microstructure of AZ91 alloy

The microstructure of as-cast AZ91 alloy is shown in Fig. 1. It was mainly composed of primary $\alpha$-Mg phase, eutectic magnesium phase (it consists of eutectic $\alpha$ and $\beta$ phase) and $\beta$ phase ($\text{Mg}_{17}\text{Al}_{12}$) locating at the grain boundary. A small quantity of $\text{AlMn}$ phase particles precipitated inside grains.3–6) Al concentration increases from the

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**Fig. 2** Apparent stress-strain curve of the uncharged and charged AZ91 alloy tested in 0.1 kmol/m$^3$ $\text{Na}_2\text{SO}_4$ solution.

**Fig. 3** The fractographies of as-cast AZ91 alloy tested in 0.1 kmol/m$^3$ $\text{Na}_2\text{SO}_4$ solution: (a) and (b) the uncharged AZ91 alloy; (c) and (d) the charged AZ91 alloy.

**Table 1** The mechanical properties of as-cast AZ91 alloy in 0.1 kmol/m$^3$ $\text{Na}_2\text{SO}_4$ solution.

<table>
<thead>
<tr>
<th>States</th>
<th>Properties</th>
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<tbody>
<tr>
<td></td>
<td>maximum stress (MPa)</td>
</tr>
<tr>
<td>the uncharged AZ91 tested in solution</td>
<td>83</td>
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<tr>
<td>the charged AZ91 tested in solution</td>
<td>73</td>
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</table>

<table>
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<tr>
<th>Decrease of mechanical properties compare to the uncharged sample</th>
<th>decrease of maximum stress (%)</th>
<th>decrease of elongation (%)</th>
<th>decrease of ROA (%)</th>
<th>decrease of TOF (%)</th>
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<td></td>
<td>12</td>
<td>18</td>
<td>27</td>
<td>2</td>
</tr>
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8) Investigation of Stress Corrosion Cracking Behaviors of an AZ91 Magnesium Alloy in 0.1 kmol/m$^3$ $\text{Na}_2\text{SO}_4$ Solution 1053
3.2 Apparent stress-strain curve

The apparent stress-strain curves of the uncharged and charged AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution are illustrated in Fig. 2. After hydrogen charging, both the maximum stress and elongation of the charged samples slightly decreased compared with the uncharged. The changes of mechanical properties of AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution are depicted in detail in Table 1. The maximum stress, elongation, reduction of area (ROA) and time to fracture (TOF) of the charged specimens reduced 12%, 18%, 27% and 2% respectively compared to those of the uncharged samples. Therefore, the overall properties of the charged AZ91 alloy was little worse than those of the uncharged, indicating that cathodic charging had little influences on the mechanical properties of AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution.

3.3 Fractography and cross section observation

The fractographies of the uncharged and charged AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution are illustrated in Fig. 3. Regardless that the samples were cathodic charged or...
not, they were characteristic of brittle large-plane cleavage fracture (in Fig. 3(a) and (c)), which were more evident at high magnifications (in Fig. 3(b) and (d)). Secondary transgranular crack (STGC) with the length of about 150 μm only emerged on the charged specimens (the arrow showed in Fig. 3(d)).

The cross section morphologies of the uncharged and charged specimens tested in 0.1 kmol/m³ Na₂SO₄ solution are illustrated in Fig. 4. Both the uncharged and charged specimens were transgranular stress corrosion cracking (TGSCC) failure (in Fig. 4(a) and (c)). STGC initiating at β phase located on surface or at interior of matrix (in Fig. 4(b), (c) and (d)). But the length of STGC of the charged samples (more than 1 cm) was about tenth times than that of the uncharged (about 100 μm). Under load, the micro-cracks that nucleated at β phase connected into a large-scale crack. The main crack propagated by coalescing the micro-crack ahead (in Fig. 4(e)).

4. Discussion

In our previous work,3,5) it was found that when the specimens were cathodically charged, hydrogen, which reduced at the interfaces of matrix and solution, diffused through the corrosion products, enriched at some locations such as β phase, reacted and formed magnesium hydride, which has been demonstrated by SIMS observation (in Fig. 5). Owing to the incoherence of hydride and β phase, hydrogen atoms could gather at the interfaces of hydride and β phase, and combine into hydrogen gas. The gathering hydrogen gas would form local high pressure. Due to the synergistic effect of high local pressure and expansion stress due to the formation of magnesium hydride, brittle hydride would be cracked (in Fig. 6).

According to Winzer,7) the increase of the hydrogen concentration difference between the interfaces of AZ91 alloy and electrolyte and matrix would cause the promotion of hydrogen flux. So at the same test time, hydrogen diffusion flux of the charged samples would be smaller due to the lower concentration gradient (between matrix and interfaces) compared with that of the uncharged. It might be offset by the cathodic charging before test. Moreover, the diffusion coefficient of hydrogen in magnesium (4.061 × 10⁻¹⁰ m²/s at room temperature11)) was small. When the hydrogen concentration at the interfaces reached a critical value, the hydrogen content at interior of matrix would be stable, which was confirmed by the Cheng’s results on pipeline steel.12) As a result, the mechanical properties of the uncharged and charged AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution were close (in Fig. 2 and Table 1). It was embodied on the fractography that both of them were brittle large-plane cleavage fracture (in Fig. 3), and on the processes of crack initiation and propagation that micro-cracks both initiated at β phase, and propagated into main crack; main crack propagated by coalescing the micro-crack ahead (in Fig. 4). Therefore, regardless of cathodic charging, the crack initia-
tion and propagation mechanisms, fractographic morpholo-
gies and mechanical properties of AZ91 alloy tested in
0.1 kmol/m³ Na₂SO₄ solution were similar. It indicated
that they had the same SCC mechanism, HE mechanism.
However, cathodic charging before test caused the formation
of hydride and the existing of micro-cracks on surface and at
interior. Moreover, the diffusion of hydrogen caused by
corrosion reaction during test would also promote the
formation and propagation of micro-crack by the synergistic
effect of high local pressure of hydrogen combination and
expansion stress of magnesium hydride formation. So the
critical stress and the mechanical properties for the charged
AZ91 alloy tested in 0.1 kmol/m³ Na₂SO₄ solution would be
lower than those of the uncharged. It was in agreement with
the results in Fig. 2 and Table 1.

5. Conclusions

The SCC behavior of an as-cast AZ91 magnesium alloy in
0.1 kmol/m³ Na₂SO₄ solution was investigated using SSRT.
The results showed that both the uncharged and charged
AZ91 alloy occurred transgranular stress corrosion cracking
(TGSCC), which were characteristic of large-plane cleavage
fracture. Pre-charging had little influences on mechanical
properties. It indicated that HE was the main mechanism
for the SCC of AZ91 alloy in 0.1 kmol/m³ Na₂SO₄ solution.

Acknowledgement

The authors would like to thank Prof. A. Atrens and Dr. N.
Winzer for providing AZ91 alloy ingots. The work is funded
by the Hundred Talent Project and NSFC Project 50499336.
The authors acknowledge the assistance.

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Fig. 6 Evolution of crack initiation using BSE detector after wetting for: (a) 0 cycle; (b) 3 cycles; (c) 6 cycles; and (d) the high
magnification of Fig. 6(c) (1 cycle was equal to 1 h wetting time and 10 min drying time while wetting pressure was 864.5 Pa and drying
pressure was 279.3 Pa).6)