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Hydrogen Embrittlement Type Stress Corrosion Cracking Behavior of Wrought Magnesium Alloy AZ31

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Abstract

Stress corrosion cracking (SCC) behavior of wrought magnesium alloy, AZ31, was investigated. SCC tests were performed using compact tension (CT) specimens in 3%NaCl solution under hydrogen charged conditions, where the cathodic potentials were -1.4, -2.5 and -3.0V. According to Pourbaix diagram, the cathodic potentials of -2.5 and -3.0V correspond to the immunity region. Under the immunity condition, hydrogen embrittlement (HE) type SCC occurred where the $K_{Iscc}$ value was much higher than that of active path corrosion (APC) type SCC. The $K_{Iscc}$ value decreased and the crack propagation rates, $da/dt$, increased with decreasing cathodic potential in the immunity region where HE type SCC occurred. At the cathodic potential of -3.0V, $da/dt$ was insensitive to the stress intensity factor.

Keywords: Magnesium alloy; Stress corrosion cracking; Hydrogen embrittlement; Crack propagation rate

1. Introduction

Magnesium (Mg) alloys have excellent properties such as light weight, high specific strength and stiffness, machinability and recyclability. These advantages make Mg alloys very attractive as structural materials in a wide variety of applications, in particular, as components for aero planes or ground vehicles, in which saving weight is extremely important. The major drawback of this alloy is poor corrosion resistance compared with other light metals such as aluminum and titanium alloys. Hence it is very important to understand corrosion properties of Mg alloys in order to apply these alloys to structural components, so that many researches have been performed with regard to corrosion [1], corrosion fatigue [2, 3] and stress corrosion cracking (SCC) [4-7]. Especially, SCC behavior of Mg alloy is widely investigated because SCC brings about unexpected sudden failure of structures.

Most of the investigations about SCC in Mg alloys are based on slow strain rate (SSR) testing [5-7], in which SCC susceptibility of materials could be easily evaluated. However, from the view point of designing of mechanical components, quantitative analysis of crack propagation rates based on fracture mechanics is inevitable, which should be estimated by SCC tests using specimens with long cracks such as compact tension (CT) and center-cracked panel specimens. In addition, SCC is generally classified into two types, namely, active path corrosion (APC) type and...
hydrogen embrittlement (HE) type. Anodic dissolution is dominant in APC type SCC, while hydrogen embrittlement is a controlling factor in HE type SCC. In many works about SCC of Mg alloys, APC type SCC is widely investigated, while there are very few works about HE type SCC. This study focuses on the stress corrosion cracking (SCC) behavior of wrought magnesium alloy, AZ31. SCC tests were performed using CT specimens in 3%NaCl solution under hydrogen charged conditions. By controlling the cathodic potentials, HE type SCC was induced and SCC behavior was investigated.

2. Experimental procedure

2.1. Material and specimen configuration

The material used is wrought magnesium alloy, AZ31, whose microstructure is shown in Fig.1. The chemical composition (mass %) is Al: 2.7, Zn: 0.79, Mn: 0.44, Fe: 0.0012, Ni: 0.0009, Cu: 0.0011, Si: 0.004, Ca: 0.001, Sn<0.001, Mg: bal. The mechanical properties are summarized in Table 1. Figure 2 shows the CT specimen configuration according to ASTM E647 standard. The CT specimens were cut from the as-received AZ31 plates with a thickness of 6mm.

Table 1. Mechanical properties

| Property            | 0.2% proof stress $\sigma_{0.2}$ (MPa) | Tensile strength $\sigma_b$ (MPa) | Elongation $\delta$ (%) | Vickers hardness $HV$ | Elastic modulus $E$ (GPa) | Grain size $d$ (\&m) |
|---------------------|--------------------------------------|---------------------------------|-------------------------|-----------------------|--------------------------|----------------------|
| Value               | 170                                  | 248                            | 17                      | 54                    | 46                       | 29                   |

Fig. 1. Microstructure of AZ31

Fig. 2. CT specimen configuration

2.2. Stress corrosion cracking test

Prior to SCC tests, pre-crack with a length of 2mm was introduced from the artificial notch root of CT specimen by a fatigue test at a frequency of 10Hz, stress ratio of 0.1 and the initial $\Delta K$ value of 3MPam$^{1/2}$. SCC tests were performed in 3%NaCl solution. SCC test specimens with fatigue pre-crack were attached to the creep testing machine equipped with 3%NaCl solution tank as shown in Fig.3. Ag/AgCl and Pt electrodes were used for reference and counter electrodes, respectively. The cathodic potentials during SCC tests were controlled to be -1.4, -2.5 and -3.0V by means of a potentiostat. It should be noted that the cathodic potentials of -2.5 and -3.0V correspond to the
immunity region according to Pourbaix diagram shown in Fig. 4. Crack length was monitored by a crack gauge bonded to a crack-expected part of CT specimen. SCC test specimens were held in 3%NaCl solution at a given cathodic potential for 24h under no-load condition in order to charge hydrogen. The initial value of $K$ was about 7MPam$^{1/2}$, and the load was gradually increased every 24h until crack started to propagate.

Figure 5 shows the relationship between crack propagation rate, $da/dt$, and stress intensity factor $K$. The critical values of $K$ for crack propagation, namely $K_{isc}$, are 8.6, 19 and 14MPam$^{1/2}$ for the cathodic potentials of -1.4, -2.5 and -3.0V, respectively, indicating that the critical values are much higher in the immunity region. It is noteworthy that the critical value at -3.0V was lower than that at -2.5V. The crack propagation rates are much faster in the corrosion region (-1.4V) than in the immunity region (-2.5 and -3.0V). In the immunity region, the crack

3. Results

Figure 5 shows the relationship between crack propagation rate, $da/dt$, and stress intensity factor $K$. The critical values of $K$ for crack propagation, namely $K_{isc}$, are 8.6, 19 and 14MPam$^{1/2}$ for the cathodic potentials of -1.4, -2.5 and -3.0V, respectively, indicating that the critical values are much higher in the immunity region. It is noteworthy that the critical value at -3.0V was lower than that at -2.5V. The crack propagation rates are much faster in the corrosion region (-1.4V) than in the immunity region (-2.5 and -3.0V). In the immunity region, the crack
propagation rates are faster at the cathodic potential of -3.0V than at -2.5V. Furthermore, it seems that the crack propagation rates are insensitive to the value of stress intensity factor at -3.0V.

Figure 6 reveals SEM micrographs of typical fracture surfaces at different cathodic potentials. Facture surface is covered by corrosion products at -1.4V. On the contrary, corrosion products are not recognized on the fracture surfaces at -2.5 and -3.0V. It indicates that APC type SCC due to anodic dissolution occurred at the cathodic potential of -1.4V, while HE type SCC without anodic dissolution took place at -2.5 and -3.0V. It is reasonable according to Pourbaix diagram. The fracture surfaces in the immunity regions are covered with packets with fine steps whose sizes appear to coincide with the grain size. This appearance is very similar to transgranular, quasi-cleavage fracture surface morphology observed under environmentally-induced cracking conditions [4].

4. Discussion

As shown in Fig.5, the $K_{I_{SCC}}$ value was much lower in the corrosion region than those in the immunity region where anodic dissolution does not occur. It indicates that APC type SCC exhibits lower $K_{I_{SCC}}$ than HE type SCC. In the immunity region without anodic dissolution, $K_{I_{SCC}}$ was lower at -3.0V than that at -2.5V. Based on Pourbaix diagram, generation of H$_2$ should be more prominent at lower cathodic potential, indicating that hydrogen charging was accelerated at the lower cathodic potential of -3.0V. Consequently, lower $K_{I_{SCC}}$ at -3.0V could be attributed to larger amount of hydrogen charging.

SCC fracture surfaces are similar between -2.5 and -3.0V as shown in Fig.6(b) and (c). It implies that fracture mechanism operated is irrelevant to the cathodic potential in the immunity region, where HE type SCC occurs. Therefore, the higher crack propagation rates at -3.0V than at -2.5V could also be attributed to larger amount of hydrogen charging as mentioned above. At the cathodic potential of -3.0V, the crack propagation rates seem to be insensitive to stress intensity factor. High amount of hydrogen charging occurred at -3.0V, and resulted in distinct HE type SCC. It is considered that brittle fracture of HE type SCC strongly depends on the amount of hydrogen charging, and consequently, the effect of stress intensity factor on crack propagation rates decreased relatively. Although the $K_{I_{SCC}}$ value was 14MPam$^{1/2}$ at -3.0V, it should be noted that $K_{I_{SCC}}$ might be further decreased by higher amount of hydrogen charging than that at -3.0V.

5. Conclusion

SCC tests of wrought Mg alloy, AZ31, were performed in 3%NaCl solution under the controlled cathodic potentials of -1.4, -2.5 and -3.0V. HE type SCC occurred in the immunity region (-2.5 and -3.0V), where corrosion products were not recognized on the fracture surfaces. The $K_{I_{SCC}}$ value for APC type SCC was much lower than that for HE type SCC. In the immunity region, the $K_{I_{SCC}}$ value became lower and crack propagation rates became higher with decreasing the cathodic potential. It could be attributed to higher amount of hydrogen charging at the lower cathodic potential. Crack propagation rates were insensitive to stress intensity factor at -3.0V due to the brittle nature of HE type SCC fracture.

![Fig. 6. SEM micrographs of fracture surface in 3%NaCl solution: (a) -1.4V, $K=18.1$ MPam$^{1/2}$, (b) -2.5V, $K=20.9$ MPam$^{1/2}$, (c) -3.0V, $K=17.6$ MPam$^{1/2}$](image-url)
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