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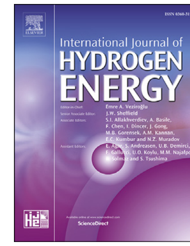

Stress corrosion cracking behavior of ZK60 magnesium alloy under different conditions

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ABSTRACT

The stress corrosion cracking (SCC) behavior of ZK60 magnesium alloy was investigated under different conditions, i.e. thin electrolyte layer (TEL) and solution, by slow strain rate tensile tests, electrochemical techniques, Auger electron spectroscopy, scanning electron microscopy coupled with electron backscattered diffraction, and time of flight secondary ion mass spectrometry. Results indicated that the ZK60 magnesium alloy in solution exhibits a higher SCC susceptibility with a combined SCC mechanism of weaker anodic dissolution (AD) and stronger hydrogen embrittlement (HE) compared to under TEL. Moreover, the HE mechanism under various conditions was discussed.

Introduction

Among structural materials such as steel, titanium, and aluminum alloys, etc., magnesium alloys exhibit the lowest density ($\rho \approx 1.74\ g\cdot cm^{-3}$), making them attractive for automotive and aerospace industries because of the significance of weight [1–3]. In addition, magnesium alloys also possess several other advantages, such as excellent castability, electromagnetic interference shielding, non-magnetic property and recyclability. Despite these intriguing properties, their use has historically been restricted considerably because of their chemical reactivity, making them less resistant to corrosion [4–9], corrosion fatigue [10,11], and stress corrosion cracking (SCC) [12–25]. SCC is typically related to mechanisms associated with anodic dissolution (AD) [26–29] or hydrogen embrittlement (HE) [30–38]. Several studies [17,18,24] have reported that HE is the typical mechanism of SCC in magnesium alloys. However, some others [13,14,25] have concluded that SCC in magnesium alloys is caused by the combination of AD and HE. Thus, the exact mechanism of SCC in magnesium alloys remains unclear.

Moreover, several mechanisms may simultaneously occur depending on the material and other variables (e.g., strain rate and ambient conditions). However, the two above-mentioned

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mechanisms that play a dominant role in the SCC of magnesium alloys are still controversial.

Magnesium alloys most likely suffer from atmospheric corrosion, which is an electrochemical process occurring on a metal surface covered with a thin electrolyte layer (TEL) [39]. Among all corrosion modes, the SCC behavior of metals under TEL is significantly different from that in a bulk solution [40–42]. The corrosion of magnesium alloys is thought to involve the cathodic reaction of oxygen reduction, and this cathodic process is significantly enhanced for samples tested under TEL. However, oxygen reduction is not as important as hydrogen evolution during the corrosion of alloys in solution. Thus, the associated mechanisms under TEL are possibly related to the combined effect of AD and HE, while HE is believed to be the most common mechanism for the SCC of magnesium alloys in solution. To identify the dominant mechanisms related to the SCC of magnesium alloys, and to support the increased use of magnesium alloys for stressed components in aerospace and automobile industry in the marine atmosphere, the SCC mechanisms of magnesium alloys under TEL and in solution must be systematically investigated.

Hence, with the limited knowledge about the SCC behavior of the ZK60 magnesium alloy, slow strain rate tensile (SSRT) tests are conducted using the ZK60 magnesium alloy under TEL and in solution. In addition, the surface appearance and fractography of all samples were observed by scanning electron microscopy (SEM); the surface film was examined using high-resolution Auger electron spectroscopy (AES); the cracking mode was characterized by electron backscattered diffraction (EBSD); and the distribution of elements in the vicinity of cracks was examined by time-of-flight secondary ion mass spectroscopy (ToF-SIMS). The results of this study may provide a comprehensive understanding on the dominant SCC mechanisms of magnesium alloys under different conditions.

Experimental

Materials and environment

Commercial ZK60 Magnesium alloy with a nominal composition of Mg–6Zn–0.5Zr (wt%) was used. Inductively coupled plasma–atomic emission spectroscopy analysis of the as-received alloy revealed a Zr content of 0.34 wt%. This value is close to the low limit for alloys with this denomination. Table 1 summarizes the chemical composition.

The experiment device shown in Fig. 1 comprised a test medium, maintained at ambient temperature (approximately 25 °C), of a modified simulated TEL atmosphere, which facilitated easy oxygen transfer. The solution in the atomizer was 0.1%NaCl + 0.05%Na_2SO_4 + 0.05%$CaCl_2$ with a pH of approximately 5.1 related to CO_2 dissolution. By contrast, the test medium in the solution was the same as that in the atomizer. However, the transfer of oxygen in solution was weaker; hence, the HE effect is possibly stronger than that under TEL.

Samples for stereoscopic microscope observations were mechanically polished to 1 μm using ethanol-based diamond suspensions followed by chemical etching using a solution of 5 g picric acid + 5 g acetic acid + 20 mL distilled water + 100 mL anhydrous ethanol. Similarly, the samples for EBSD characterization were mechanically polished and electropolished using 10% perchloric acid in ethanol at 0 °C and at a polishing voltage of 15 V for 30 s. The EBSD samples were observed in the vicinity of the cracks. Automatic EBSD scans were recorded using TSL data acquisition software with a step size of 1 μm. The EBSD data were analyzed using TSL OIM software.

SSRT tests

SSRT tests were carried out to investigate the SCC behavior of ZK60 alloy under different conditions. A flat-plate tensile specimen was prepared based on GB/T 15970 [43]. Prior to each SCC test, the tensile samples were prepared from electro-discharge machining. The samples were successively ground using silicon carbide papers up to 2000 grit, ultrasonically cleaned in absolute ethanol for 10 min, and dried under a flow of cool air.

SSRT tests were carried out on a WDML-30kN Materials Test System with a strain rate of $1 \times 10^{-6}\ s^{-1}$ (Fig. 1a). Before each test, the specimen was maintained under 100% RH for 1 h to ensure the formation of an electrolyte film on the surface. Moisture was continuously pumped during the entire experiment. After failure, one piece of the fracture was analyzed for characterization, and the other was applied for the measurement of the hydrogen concentration. First, the percentage of elongation and area reduction of each specimen were calculated after the removal of corrosion products. In addition, fracture morphologies were observed by SEM. Each test was reproduced at least three times to ensure the reliability of experimental data, and the standard deviation of the data was measured. Next, the cross-sectional morphologies of the fracture were observed to investigate the localized corrosion severity and cracking mode. Moreover, the hydrogen concentration of the tested samples was measured using a hydrogen analyzer (G4 Phoenix DH).

Electrochemical measurements

Fig. 1b shows the measurement system comprising the typical three-electrode system. The working electrode is ZK60 specimen with a working area of 1 cm^2, the counter electrode is a Pt bulk circling around the working electrode, and the

Table 1 – Chemical composition of the ZK60 magnesium alloy.

Alloy	Chemical composition (mass%)								
	Al	Zn	Mn	Fe	Si	Cu	Ni	Zr	Mg
ZK60	–	5.12	0.02	0.0024	0.003	0.0019	0.0011	0.34	Bal.

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