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Full length article

Effect of hydrogen on the corrosion behavior of the Mg–xZn alloys

Yingwei Song [a,*], En-Hou Han [a,*], Kaihui Dong [a], Dayong Shan [a], Chang Dong Yim [b], Bong Sun You [b]

[a] *Key Laboratory of Nuclear Materials and Safety Assessment, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China*
[b] *Korea Institute of Materials Science, Changwon 641-831, Republic of Korea*

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Abstract

Hydrogen evolution reaction is inevitable during the corrosion of Mg alloys. The effect of hydrogen on the corrosion behavior of the Mg–2Zn and Mg–5Zn alloys is investigated by charging hydrogen treatment. The surface morphologies of the samples after charging hydrogen were observed using a scanning electron microscopy (SEM) and the corrosion resistance was evaluated by polarization curves. It is found that there are oxide films formed on the surface of the charged hydrogen samples. The low hydrogen evolution rate is helpful to improve the corrosion resistance of Mg alloys, while the high hydrogen evolution rate can increases the defects in the films and further deteriorates their protection ability. Also, the charging hydrogen effect is greatly associated with the microstructure of Mg substrate.

Keywords: Charging hydrogen; Corrosion resistance; Mg–xZn alloys; Oxide films

1. Introduction

Mg and its alloys are the lightest structure materials with high chemical activity. They are susceptible to corrosion at the actual applications [1]. Because the standard potential of pure Mg ($E^0 = -2.4\ V_{NHE}$) is much more negative than that of hydrogen reduction, it will take place hydrogen evolution reaction at the cathodic sites during the corrosion of Mg alloys [2]. In the meantime, Mg and its alloys exhibit the special features of Negative Difference Effect (NDE) and "anodic hydrogen evolution" [3,4]. The hydrogen evolution reaction will be accelerated with increasing anodic potentials. Thus, the hydrogen evolution reaction is inevitable regardless of at cathodic and anodic regions (Cathodic reaction: $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$; Anodic reaction: $Mg + 2H_2O \rightarrow Mg^{2+} + H_2 + 2OH^-$ [5]). In the case of other metal materials, plenty of research results indicate that hydrogen has a very important effect on their corrosion behavior [6,7]. Hydrogen gas can permeate into the interior of metals then gather, initiating the hydrogen embrittlement phenomenon. Also, there are some studies about the effect of hydrogen on the corrosion behavior of Mg alloys. Chen et al. [8,9] found that hydrogen can result in the crack of β phases and initiation of stress corrosion crack (SCC) on AZ91 Mg alloy. Bakkar et al. [10] permeated hydrogen into Mg alloys by EIR and PIII techniques and found that the corrosion resistance of Mg alloys was improved. The research results of Zhang et al. [11] indicate that hydrogen has a dual effect on the corrosion behavior of Mg alloys. If the concentration of hydrogen is low, it can reduce the defect density of surface films and improve the corrosion resistance. On the contrary, if the content of hydrogen is high, hydrogen can deteriorate the stability of surface films and decrease the corrosion resistance. In a word, there are not consistent opinions about the

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* Corresponding authors. Tel.: +86 24 23915772; fax: +86 24 23894149.
E-mail addresses: ywsong@imr.ac.cn (Y. Song), ehhan@imr.ac.cn (E.-H. Han).

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function of hydrogen on the corrosion behavior of Mg alloys. Also, the effect of microstructure on the charging hydrogen effect is not clear. Thus, the surface oxide films and corrosion resistance of the Mg−2Zn and Mg−5Zn alloys after charging hydrogen treatment are investigated, aiming to disclose the role of hydrogen in the corrosion process of Mg alloys.

2. Experimental

The experimental materials used for this investigation were the extrusion Mg−2Zn and Mg−5Zn plates which were provided by Korea Institute of Materials Science (KIMS) as reported in the previous paper [12−14]. The samples were successively ground to 3000 grit paper, cleaned in alcohol, and then dried in cool air. The samples for metallographic observation were further ground to 5000 grit paper, finely polished using 1 μm diamond paste and then etched by the solution consisting of 1 g oxalic acid, 1 mL nitric acid, 1 mL acetic acid and 150 mL distilled water.

The Mg−2Zn and Mg−5Zn alloys were charged hydrogen in 0.1 M NaCl solution (pH 6.2) at the cathodic currents of −1, −5 and −10 mA for 2 h using an EG&G potentiostat model 273 (Princeton Applied Research, USA). A classical three−electrode cell was used, with a platinum plate as counter electrode, a saturated calomel electrode as reference electrode and the sample with an exposed area of 1 cm^2 as work electrode. The potentials of the charged hydrogen samples were recorded during the charging hydrogen process. 0.1 M NaCl solution was renewed after charging hydrogen, and then the polarization curve measurements were carried out immediately. The polarization measurements started from −200 mV below open circuit potential at a constant scan rate of 0.5 mV s^{-1} and were terminated until a fast increase of the anodic current density. An initial delay of 300 s was set before the polarization curve measurements. At least three electrochemical measurements were performed under the same testing conditions for ensuring the reproducibility. The polarization curves were fitted using CorrView software.

The surface morphologies of the samples after charging hydrogen treatment were observed using a Phillips XL30 scanning electron microscopy (SEM) equipped with an energy dispersive X-ray spectroscopy (EDX).

3. Results and discussion

The microstructures of the Mg−2Zn and Mg−5Zn alloys are shown in Fig. 1. Although their microstructures have been reported in our previous papers [12−14], they are shown again aiming to compare their surface morphologies with the samples after charging hydrogen treatment. In the case of the Mg−2Zn alloy, the alloying element of Zn is completely dissolved into Mg matrix and there are no precipitation phases observed. Differently, some of Zn is dissolved into Mg matrix and the rest is precipitated on the grain boundaries of the Mg−5Zn alloy. The Mg−2Zn alloy exhibits better corrosion resistance than the Mg−5Zn alloy [14].

The Mg−2Zn and Mg−5Zn alloys were charged hydrogen at the cathodic currents of −1, −5 and −10 mA for 2 h. From the optical observation of the samples during the charging hydrogen treatment, plenty of hydrogen gas bubbles escaped from the surface of Mg alloys. The hydrogen generation rate promotes with increasing cathodic charging currents. Fig. 2 shows the development of potentials with increasing cathodic charging hydrogen time of Mg−2Zn. The larger the charging hydrogen currents are, the more negative the potentials of the samples become. The development trends of the potentials can be divided into three stages. The potentials first rise in stage I and then decline in stage II, and finally tend to rise slowly in stage III except for the sample charged hydrogen at −1 mA which keeps a stable level. The slow rise of potentials in stage III means that the chemical stability of the samples is improved gradually [15]. The sample charged hydrogen at −10 mA exhibits the highest growth rate of potential in stage III, while the sample charged hydrogen at −1 mA exhibits the smallest one. Based on this case, it can conclude that the chemical stability of the Mg alloys is promoted with increasing cathodic charging hydrogen currents from −1 to −10 mA.

The surface morphologies of the Mg−2Zn alloy charged hydrogen at various cathodic currents for 2 h are shown in Fig. 3. It can find that the oxide films consisting of sheet particles are visible on the surface of the Mg−2Zn after charging hydrogen treatment. With increasing cathodic currents, the coverage percents of the oxide films increase. The oxide films are thin. But they are more obvious in the scratch

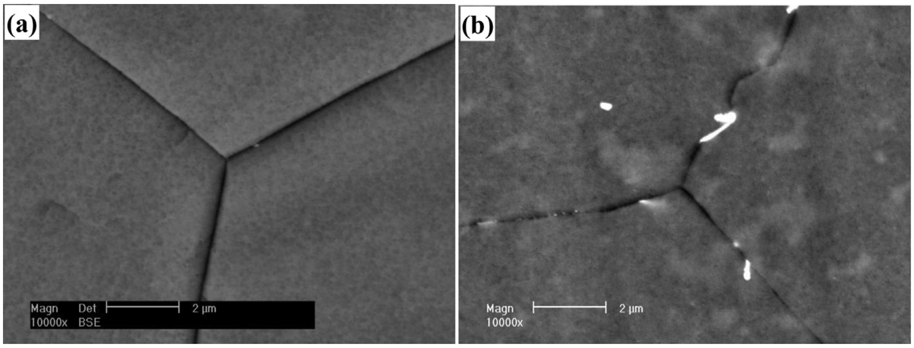

Fig. 1. Microstructure of (a) Mg−2Zn and (b) Mg−5Zn alloys.