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Electrochemical noise analysis of the corrosion behaviors of Al-Zn-In based alloy in NaCl solution

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Abstract

The corrosion behaviors of Al–5Zn–0.02In–1Mg–0.05Ti (wt. %) alloy immersion in 3.5% NaCl solution were analyzed using electrochemical noise. At the initial immersion, the potential noise due to the pitting shows small fluctuation of less than 1 mV about 5 s intervals. After 10 h immersion, the potential noise due to the dissolution/precipitation shows larger fluctuation about 5 mV at 10 s intervals. In the later corrosion, the potential noise caused by the uniform corrosion shows the fluctuation about 10 mV at 60 s intervals.

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Keywords: Aluminum alloys; Corrosion; Electrochemistry

1. Introduction

Aluminum alloys are widely used as sacrificial anode materials in cathodic protection. There is little doubt today that Al–Zn–In anodes present the best performance in seawater. The current efficiency of Al–Zn–In–Mg–Ti alloys were found to be exceeding 90%, so these alloys have became popular in China (Zhang et al., 2011, Huang et al., 2011). But there are few data in the literature about the corrosion behavior about the alloys. The paper (Ma et al., 2009) investigated the effects of Mg and Ti on the microstructure and electrochemical performance of Al–5Zn–0.02In–1Mg–0.05Ti (wt. %) alloy. The other paper (Ma et al., 2010) surveyed the corrosion behaviors of the alloy in 3.5 wt. % NaCl solution by electrochemical impedance spectroscopy.

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The spontaneous fluctuations of the corrosion potential and the corrosion current, observed during open-circuit for metals are termed electrochemical noise (EN) (Curioni et al., 2011, Rauf et al., 2012, Na et al., 2008). These fluctuations have been associated with the initiation of localized corrosion (Kiwilszo et al., 2009, Liu et al., 2008, Na et al., 2008). Pitting is a stochastic process. Noise analysis can provide detailed information about the pit initiation and propagation stages (Lafront et al., 2010, Na et al., 2007, Sasaki et al., 2002). EN gained popularity in the recent years and has emerged as a promising technology for corrosion analysis. EN can be performed in situ to monitor the corrosion processes and can provide more information of localized corrosion than conventional techniques(meng et al., 2009, Sanchez-Amaya et al., 2005). In this study, the potential fluctuations of Al–5Zn–0.02In–1Mg–0.05Ti (wt. %) alloy at different corrosion stages have been monitored in 3.5 wt. % NaCl olution. The potential fluctuation during corrosion is analyzed by the experimental results to gain a better understanding of the corrosion mechanism.

2. Experimental

The nominal compositions of alloy in present experiment is 5 wt.% Zn–0.02 wt.% In–1 wt.% Mg–0.05 wt.% Ti–Al. Raw materials are commercial pure aluminum, zinc, indium, magnesium, titanium ingots (>99.9%) for casting the above anode alloy. Raw material ingots were cut, dried, weighed the required amount of materials and melted in a graphite crucible in ZGJL0.01-4C-4 vacuum induction furnace under argon atmosphere at 760±10 ℃.The molten alloy was poured in a preheated cast iron dye of dimensions ⊄ 20 mm×140 mm.

The samples of immersion tests were ground with emery paper (grade 400-800-1000-2000) and polished with 2.5 and 1.5 μm diamond pastes. A few samples were immersed in 3.5% NaCl solutions contained in a different beaker at the same time. The numbered sample was taken out from the beaker one by one, respectively, after immersion different time. The corrosion products of the samples were clean-out in a solution of 2% CrO_3 and 5% H_3PO_4 at 80 ℃ for 5 min, then rinsed by ethanol. The corroded surface of the samples in 3.5 wt. % NaCl solution at different immersion time was examined using JSM-5610LV scanning electron microscope (SEM).

Electrochemical noise measurements were carried out in 3.5% wt. % NaCl solution at room temperature, using the CHI660A electrochemical measuring system equipped with an EN module. A standard three electrode system was used for the measurements of electrochemical noise. Two identical samples were used as the working electrode and a saturated calomel electrode (SCE) as the reference electrode. The exposed area of the working electrode was 1 cm^2. The samples were ground with emery paper (grade 400-800-1000-2000) and polished with 2.5 and 1.5 μm diamond pastes. Potential data were recorded with a sampling frequency of 1 second.

3. Results and Discussion

The microstructure of the alloy is shown in Fig. 1(a). The alloy is mainly consisted of α-Al matrix with precipitates on the grain boundaries. Fig. 1(b–d) shows the representative corroded surface of the alloy at different immersion time. No corrosion pit can be observed in Fig. 1(a). After 2 min immersion, some pits become distinguishable (Fig. 1b), and the pits formation from the precipitates. After 10 h immersion (Fig. 1c), special features can be seen showing a mud structure in grain. The uniform corrosion with numerous mud structures and pits covering the alloy surface after 3 day immersion can be detected (Fig. 1d). Before measuring the noise for corrosion systems, instrumental noise in the potential channel was determined. Fig. 2a shows a typical potential noise pattern for the alloy immersion in 3.5% NaCl solution for 2.5 hours. The potential noise decreases about 10 mV at the beginning to a minimal value, then increases. Corresponding to the morphology of the corroded alloy after 2 min immersion, pits can be detected in Fig. 1 (b), suggesting the decreased potential is due to the pitting. Yongjun (Yongjun et al., 2009) also observed the potential fluctuation characteristic of pitting initiation of carbon steel in solution containing 1000 ppm $NaNO_3$ and 4000 ppm NaCl for 10 h. Fig. 2b shows the magnification potential noise at position b in Fig. 2a and small amplitude potential fluctuation of less than 1 mV with the intervals about 5 s. This is due to the formation and repair of the pitting.

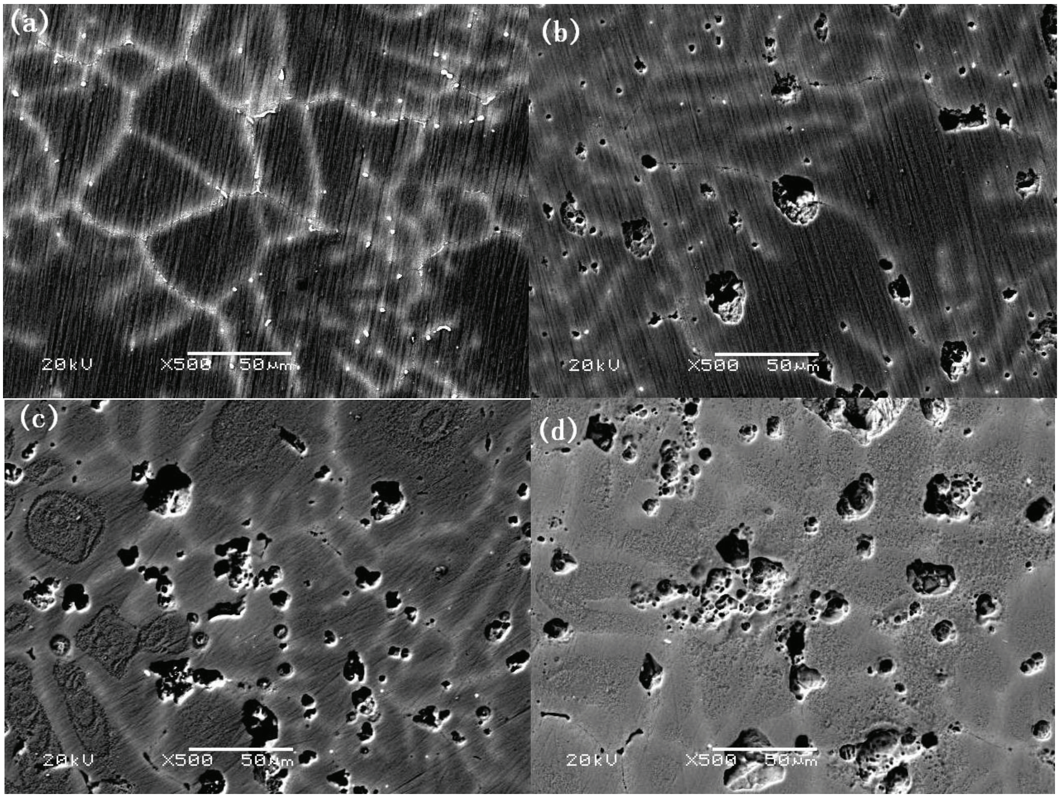


Fig. 1. The SEM imagines of Al-5Zn-0.02In-1Mg-0.05Ti (wt.%) alloy before (a) and after immersed in 3.5%NaCl solution for 2 min (b), for 10 h (c) and for 3 d (d)

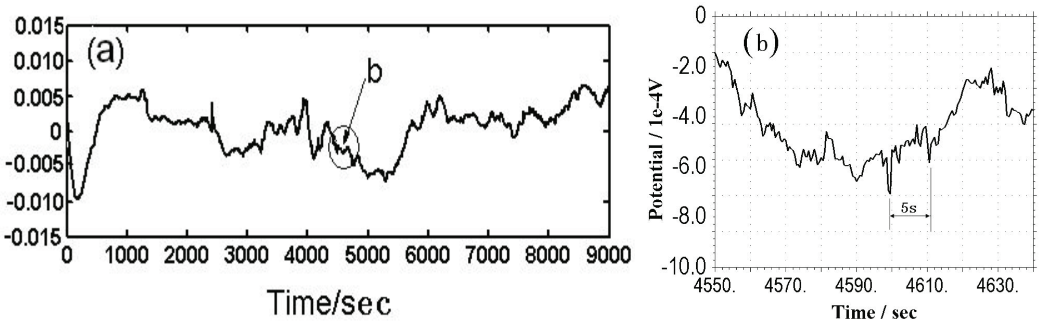


Fig. 2. Potential noise of Al-5Zn-0.02In-1Mg-0.05Ti (wt%) alloy after 2.5h immersion in 3.5%NaCl solution (a) and (b) the enlarged position shown in (a)

Fig. 3a shows a typical potential noise pattern for the alloy immersion in 3.5% NaCl solution for 10 h -12.5 h. It shows that the potential noise pattern from initial about 4000 s is similar to that in Fig. 2a. But the potential noise fluctuation increases sharply and the frequency of the noise is very high during the later 4000 s. Corresponding to the morphology of the alloy after10 h immersion, the particular corrosion morphology of mud structure can be detected besides the pitting in Fig. 1 (c). The paper [4] shown that the formation of the mud structure is involve the dissolution/precipitation of indium and zinc. The small and the large amplitude noise fluctuation appeared simultaneously indicates that the pitting and dissolution/precipitation simultaneous happening after10 h immersion.The magnification of the potential noise in Fig. 3b from 5760s shows some larger potential amplitude fluctuations about 5 mV at 10 s intervals. So the potential noise fluctuation value of the dissolution/precipitation is higher than that of pitting.

Fig. 4a shows a typical potential noise pattern for the alloy immersion in 3.5% NaCl solution after immersion 3 day. Compare with Fig. 2a and Fig. 3a, the potential fluctuation in Fig. 4a is very steady and regular and the frequency of the noise was very high. Fig. 4b and Fig. 4c show the magnification potential noise at position b and position c in Fig. 4a, respectively. Corresponding to the uniform corrosion morphology with the mud structure and the pitting of the alloy after 3 day immersion in Fig. 1 (d), the potential noise is due to the uniform corrosion. The potential noise amplitude fluctuation of the uniform corrosion shows about 10 mV at 60 s intervals.

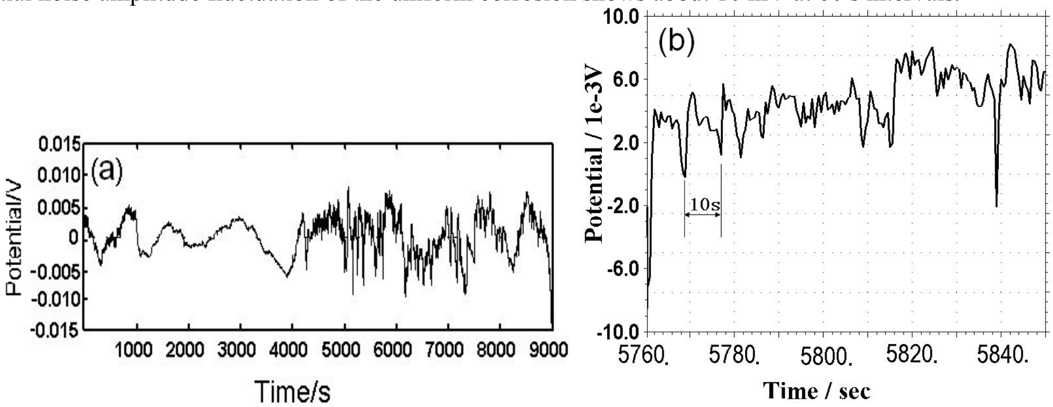
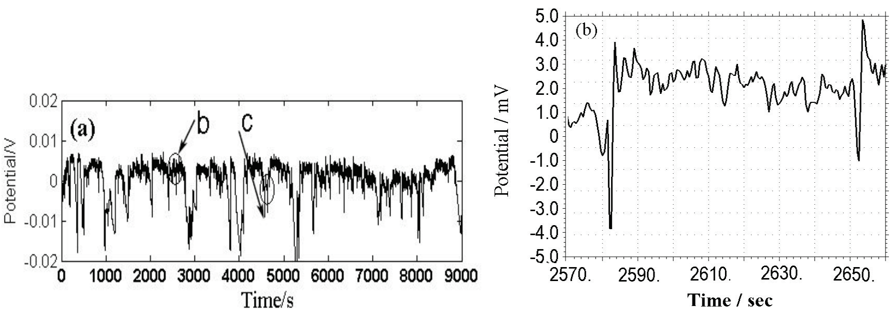


Fig. 3. (a) Potential noise of Al-5Zn-0.02In-1Mg-0.05Ti (wt%) alloy after 10h immersion in 3.5%NaCl solution and (b) the enlarged location shown in (a) after 10h +5760s immersion in 3.5%NaCl solution



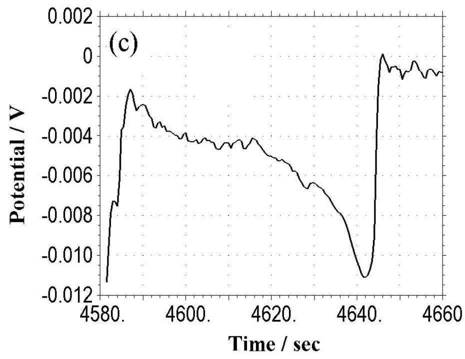


Fig. 4. Potential noise of Al-5Zn-0.02In-1Mg-0.05Ti alloy after immersion 3d in 3.5 % NaCl solution and (b), (c) magnification according to sign location b and c

4. Conclusions

In summary, we have investigated the corrosion behaviors of Al–5Zn–0.02In–1Mg–0.05Ti (wt. %) alloy after different immersion times in 3.5% NaCl solution using SEM and EN. Our findings indicate that the potential noise has significant properties on the different corrosion stages of the pitting, dissolution/precipitation and uniform corrosion. At the initial stage of immersion, the potential noise due to the formation and repair of the pitting shows small amplitude potential fluctuation of less than 1 mV with the intervals of 5 s. With increase of immersion time, the potential noise due to the dissolution/ precipitation shows amplitude potential fluctuation about 5 mV at 10 s intervals. The mud structure can be detected besides the pitting. At the later stage of immersion, the potential noise due to the uniform corrosion shows the larger amplitude potential fluctuation about 10 mV with the intervals of 60 s. The pits and the mud structure cover almost the entire alloy surface. The EN results are in good agreement with the SEM imagines.

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