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Letter

The reliability of electrochemical noise and current transients characterizing metastable pitting of Al–Mg–Si microelectrodes

L. Guan, B. Zhang *, J.Q. Wang, E.-H. Han, W. Ke

State Key Laboratory for Corrosion and Protection, Institute of Metal Research, Chinese Academy of Sciences, Shenyang 110016, China

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ABSTRACT

Current transient measurements and electrochemical noise (EN) method have been used to characterize the metastable pitting events for Al–Mg–Si microelectrodes (diameter 50 μm) in deaerated neutral 0.5 M NaCl solution. The results are compared with those obtained by atom force microscopy and scanning electron microscopy. The pit numbers determined by shot noise analysis at open circuit potential and by current transient analysis at −1.2 V (SCE) are both significantly less than those determined by corrosion morphology image analysis. These results indicate that larger discrepancies can be introduced if the anodic and cathodic reactions localize severely on the same electrode.

1. Introduction

Metastable pitting as a precursor state to stable pitting is usually characterized by tiny anodic current transients under an applied anodic potential [1–9] or between two identical specimens [10]. The pit volume can be calculated by anodic transient integration based on Faraday's law for a hemispherical pit assuming the anodic current efficiency is 100% in stainless steel [11]. Recently, Klapper et al. reported that the cathodic process plays a decisive role on the form of transients arising from pitting corrosion of stainless steel, with significant influence on the interpretation of the electrochemical noise signals [12]. This finding implies that if localized anodic and cathodic reactions severely occur at the same site during pitting corrosion, larger errors may be introduced between the true anodic pitting current and the measured one. This issue may be more important for the pitting of Al alloys, since there are many types of intermetallic cathodic particles presented in them.

To date, metastable pitting of aluminium and its alloys have been extensively investigated [6,13–15]. By using a microelectrode, the individual pitting current transient can be distinguished from the background current so that pit events can be identified [10,16]. It is generally believed that the pit events can be well analysed by the electrochemical method if the pitting is associated with the anodic particles. But for Al alloys with cathodic constituents or precipitates, Burstein et al. have detected combined anodic/cathodic current wings during polarization as a result of the presence of Al_3Fe [9]. It is therefore argued that whether the true anodic pitting current can be detected by the advanced electrochemical measurements if pitting is associated with the cathodic particles. In order to prove this, one way is to compare the true pit size and number with those measured by the current transients.

Herein, current transient behaviour under potentiostatic polarization and electrochemical noise (EN) at open circuit potential (OCP) for Al–Mg–Si microelectrodes (50 μm in diameter) is reported. The results are compared with those obtained by atom force microscopy (AFM) and scanning electron microscopy (SEM) using imaging analysis. In this way, the reliability of current transient measurements and EN to characterize the metastable pitting for an Al–Mg–Si alloy has been examined.

2. Experimental

The material used in this study is an Al–Mg–Si wire (50 μm in diameter 1.0 Mg, 0.6 Si, 0.15 Cr, 0.15 Cu, 0.7 Fe and balance Al in wt.%) from Goodfellow Cambridge Limited. The current transient measurements were conducted using a PARSTAT 4000 potentiostat equipped with low current option (VersaSTAT LC). To minimize the extraneous noise, both the electrochemical cell and VersaSTAT LC were placed in a Faraday cage and an uninterruptible power supply (UPS) was used for both the potentiostat and the computer. The

* Corresponding author. Address: 62 Wencui Rd, Shenyang 110016, China. Tel.: +86 24 23915897; fax: +86 24 23894149.
E-mail address: bxz011@imr.ac.cn (B. Zhang).

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wire was electrically connected to a copper wire with conductive silver adhesive and mounted in Struers epoxy resin. The end was initially abraded with silicon carbide papers up to 3000 grit and polished to 1 μm finish with diamond polishing paste. Then the sample was rinsed with distilled water and immediately immersed in the deaerated neutral 0.5 M NaCl solution with exposed area of about 2300 μm^2. Polarization curve measurements were conducted for at least three times with a scan rate of 0.167 mV/s. Current transient measurements were conducted at two constant applied potentials in the passive range, respectively. All potentials are referred to saturated calomel electrode (SCE). The data were collected at a sampling rate of 200 Hz. Samples were inspected after testing to verify the absence of crevice corrosion. Electrochemical tests started immediately after the immersion. All experiments were carried out at 15 ± 2 °C. Ignoring the non-Faraday process, metastable pitting volumes were obtained with the integral anodic charge for one current transient. The pitting event

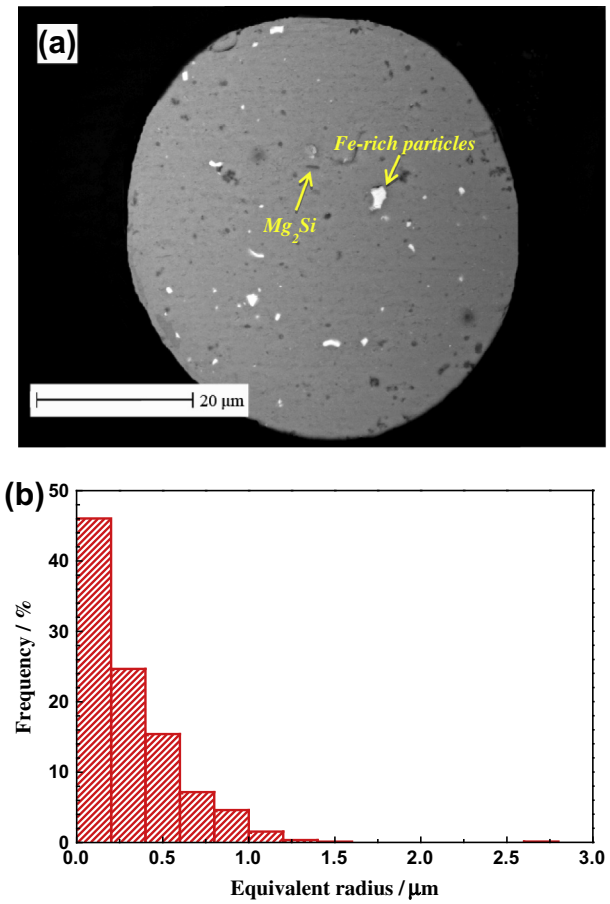

Fig. 1. The microstructure and particle size distribution of the Al–Mg–Si alloy: (a) the backscattered electron (BSE) image of the microelectrode; (b) the histogram of the Fe-rich intermetallic particle sizes.

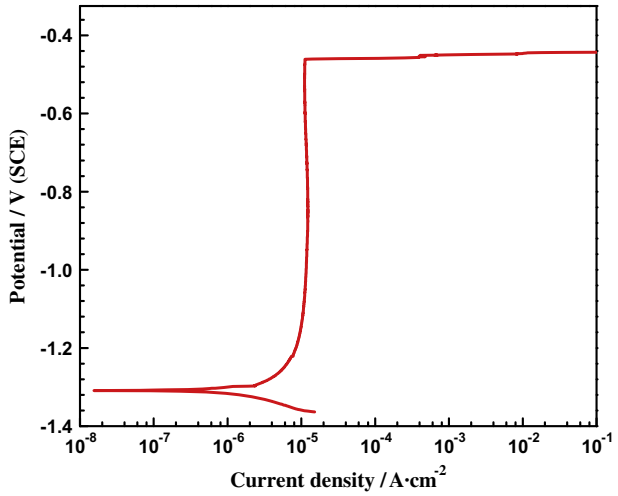

Fig. 2. A typical potentiodynamic polarization curve of Al–Mg–Si microelectrode in deaerated neutral 0.5 M NaCl solution at a scan rate of 0.167 mV s^{-1}.

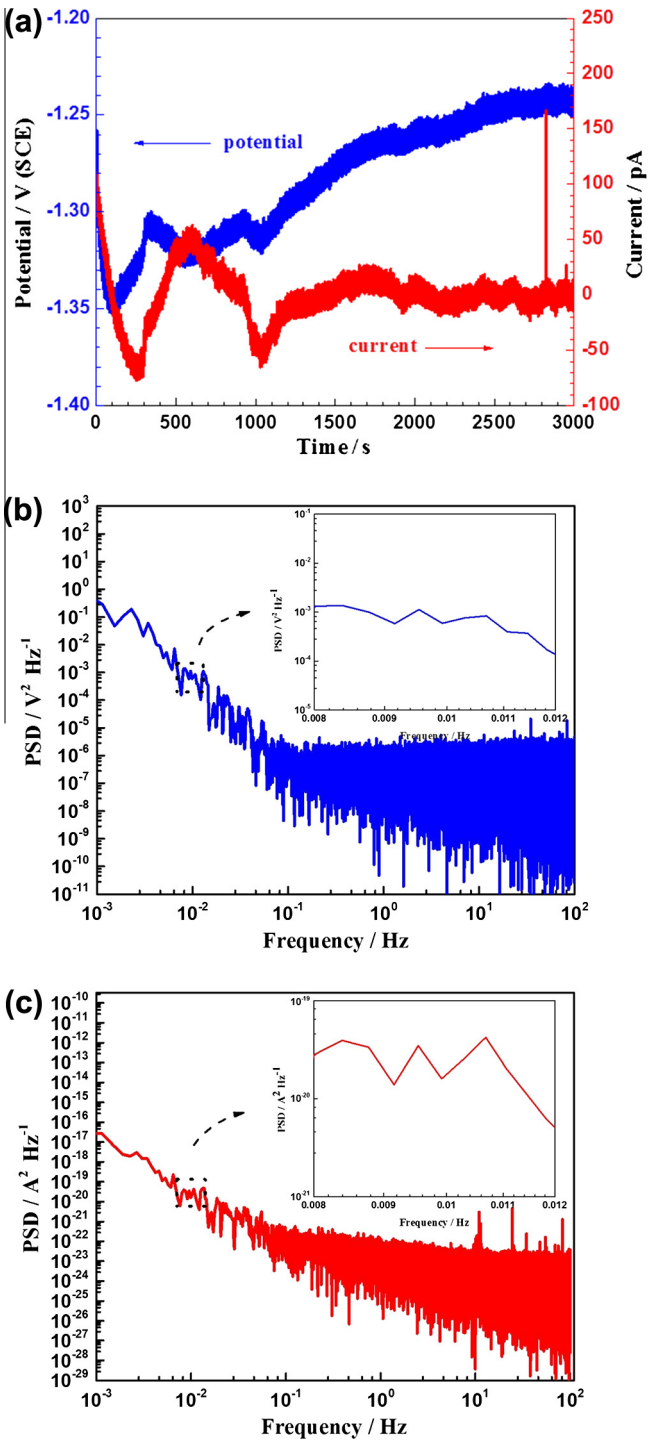

Fig. 3. Time and frequency domain spectrum of the EN for the Al–Mg–Si alloy after exposure in deaerated neutral 0.5 M NaCl solution for 3000 s: (a) electrochemical potential and current noise; (b) potential PSD plot; (c) current PSD plot.