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Letter

# Detection and analysis of anodic current transients associated with nanoscale β-phase precipitates on an Al–Mg microelectrode

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ABSTRACT

The metastable pitting of Al–5 wt%Mg microelectrode (diameter 50 μm) after aging at 150 °C for 10 h has been investigated under a constant potential in deaerated 0.6 M NaCl solution (pH 3.5). Current transients (pA size) associated with the dissolution of nanoscale β-phase precipitates have been detected. Taking the cathodic current of $H_2$ evolution inside the pit into account, the average volume determined from a charge associated with individual current transients is about 39% of those measured by TEM. This result implies that the selective dissolution of Mg in β-phase precipitates ($Al_3Mg_2$) may occur during the metastable pitting process.



## 1. Introduction

All pits, whether they proceed to the stable growth regime, or not, grow initially in the metastable state [1]. Many findings suggest that a better understanding of pit initiation, stabilization and growth may be gained from a thorough investigation of metastable pitting phenomena [2–5]. For Al alloys, it is well established that pitting is usually induced by intermetallic particles that exhibit different electrochemical activity (anodic or cathodic) to the matrix [6–12]. The metastable pitting can be characterized by anodic current transients under an applied anodic potential [1–4,9,13,14] or between two identical specimens [15]. However, from the technique point of view, the pA size metastable pitting current associated with these particles are very difficult to detect, especially for the nanoscale precipitates in many Al alloys. There are three reasons for the difficulty. Firstly, the events are very fast with the duration of several milliseconds so that they are hard to detect with a low sampling rate. Secondly, the current peaks are usually in the order of 100 pA or less. For example, the β-phase precipitate ($Al_3Mg_2$) in Al–Mg alloys is more active than the Al matrix and corrodes preferentially with a fast rate under a certain environmental conditions. The typical size of β-phase precipitate ranges from 50 to 190 nm in width and 100 to 1000 nm in length [16], correspondingly the lowest dissolved charge of the single β-phase precipitate (ellipsoid in shape) is only 2.8 pC. Thirdly, the quantity of precipitates along the grain boundaries is usually very large, and the current transients of several β-phase precipitates may overlap each other.

The use of a microelectrode [9] or micro-electrochemical technique [17] can make the background noise current very low (pA level). More importantly, both techniques can reduce the quantity of active sites and make it possible to distinguish the current transient of a single nanoscale particle. Suter et al. [17] have successfully correlated the metastable pitting with MnS precipitates in stainless steel. Speckert and Burstein [9] have detected the current transient of metastable pitting with equivalent radius of 12 nm for an aluminum alloy 1050 microelectrode at −0.35 V (Ag/AgCl). However, to date, no current transient with respect to the dissolution of a single anodic β-phase precipitate has been detected. In our previous work, it was demonstrated that the true anodic pitting current cannot be accurately detected if pitting is associated with the cathodic particles using a microelectrode [11]. Herein, we attempt to explore the relationship between current transients and the anodic β-phase precipitates through potentiostatic polarizing of Al–Mg microelectrodes (diameter 50 μm). In order to achieve this, the quantity of β-phase precipitates has been controlled by a well-defined aging treatment. By comparing the volumes of β-phase precipitates determined by the charge

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associated with single peak current transients and those measured by the scanning electron microscopy (SEM) and transmission electron microscopy (TEM), the correlation of the anodic dissolution current with nanoscale β-phase precipitates has been examined.

## 2. Experimental

### 2.1. Materials and preparation

The material used in this study is an Al–5 wt%Mg solid solution wire (diameter 50 μm, denoted as A0) from Goodfellow Cambridge Limited. It was aged at 150 °C for 10 h (denoted as A10) before electrochemical tests. The wire surfaces were cleaned with alcohol and deionized water, then dried with cold air prior to mounting. Both A0 and A10 wire were soldered to copper wire and mounted with the Struers epoxy resin (EpoFix Kit). The ends were abraded with silicon carbide papers and polished to 1 μm finish. The exposed area is approximately $1.96 \times 10^{-5}$ cm$^2$.

### 2.2. SEM and TEM characterizations

Etching of the microelectrodes was performed in 100 g/L $(NH_4)_2S_2O_8$ solution in the ambient environment. This etching method was developed by Yang et al. [18] who reported that β-phase precipitates can be visualized directly at a very fine scale. The etched morphologies were observed by SEM (Philips XL30-FEG). Precipitates formed in the A10 microelectrode were investigated by Philips CM20 TEM operated at an accelerating voltage of 200 kV. There is a challenge for the preparation of TEM samples. In this work, ten 5 mm long wires were fixed to a copper collar side by side with epoxy (ELMERS Super Fast). Then wire thinning was carried out by ion sputtering (Leica EM RES101) at 5 kV with current of 2 mA. The sputtering was carried out for 2–3 h at angle of 15° and then 3–5 h at angle of 6°. Statistical analyses of the precipitate size from both SEM and TEM images were performed by ImageJ (1.44p) software [19].

### 2.3. Current transient measurements

Potentiostatic polarization measurements were conducted using a PARSTAT 4000 potentiostat equipped with low current module (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 electrolyte of 0.6 M NaCl solution was made with analytical grade reagent and distilled water. The pH was adjusted to 3.5 by adding appropriate amounts of hydrochloric acid and sodium hydroxide. Then the solution was purged with nitrogen for at least 2 h prior to the electrochemical measurements. The polished sample was rinsed with distilled water and immediately immersed in the deaerated solution.

The potentiostatic polarization of A10 was conducted at −0.78 V (SCE) for 3600 s in the passive region (determined by potentiodynamic polarization) with the data sampling rate of 200 Hz. For comparison, A0 microelectrode was polarized at −0.72 V (SCE) in the passive region. Electrochemical tests started immediately after immersion. To prevent the noise introduced from perturbation of the solution, the purging was stopped once the measurements began. The experiment was carried out at room temperature (15 ± 2 °C). To verify the absence of crevice corrosion, samples were carefully inspected by SEM after testing.

## 3. Results and discussion

### 3.1. SEM and TEM characterization

Fig. 1a shows the back-scattered electron (BSE) image of etched A10 microelectrode. It clearly shows that there are large numbers of pits on the etched surfaces of A10 microelectrode. Most of them along the grain boundary have elliptical shape. Based on this image, the size (long and short axis are noted as $a$ and $b$, respectively) of randomly selected 25 ellipsoid pits were calculated by ImageJ. The volume can be calculated as

$$V = \frac{4\pi ab^2}{3} \quad (1)$$

Therefore, the corresponding average volume of the pits is $1.33 \times 10^{-4}$ μm$^3$. A typical image of A10 microelectrode obtained through high-angle annular dark-field imaging (HAADF) shown in Fig. 1b demonstrates that several intermetallic particles were

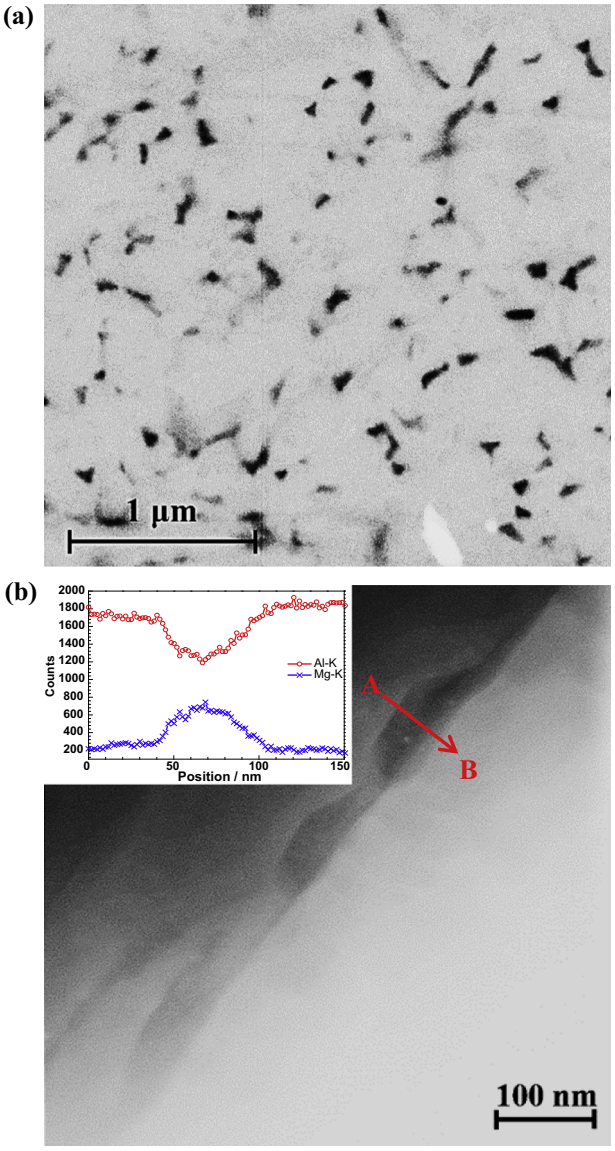


**Fig. 1.** (a) BSE micrograph showing morphology of A10 microelectrode after etching in 100 g/L $(NH_4)_2S_2O_8$ for 2.5 h at room temperature; (b) typical HAADF (high angle annular dark field) micrograph of β-phase with Al and Mg concentration profiles across the line A–B.