Electrochimica Acta 54 (2009) 6668–6673

Contents lists available at ScienceDirect

Electrochimica Acta

journal homepage: www.elsevier.com/locate/electacta

Studies of the anodic dissolution of aluminium alloys containing tin and gallium using imaging with a high-speed camera

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ARTICLE INFO

Article history:
Received 24 March 2009
Received in revised form 2 June 2009
Accepted 20 June 2009
Available online 28 June 2009

Keywords:
High-speed camera
Sn and Ga
Microelectrodes
Aluminium alloys

ABSTRACT

Imaging with a high-speed camera at a resolution of 10–20 μm has been used for the direct observation of the anodic dissolution of aluminium alloys containing Sn and Ga. The imaging allows confirmation that hydrogen bubble evolution occurs from the Sn inclusions within rounded pits during both open circuit corrosion and anodic dissolution. Using microelectrodes with only a few Sn inclusions in their surface, it is shown that the evolution of H_2 is not continuous and may be correlated with a potential oscillations between −1.50 V (where H_2 evolution occurs) and significantly less negative potentials (where no H_2 is evolved). It is proposed that this potential shift is associated with pH changes resulting from H_2 evolution itself.

1. Introduction

In an earlier paper [1], we have reported a study of the anodic dissolution of aluminium alloys containing tin and gallium in 2 M NaCl. It was shown that the high rate, steady state anodic dissolution (up to 500 mA cm^{-2}) of the alloys was possible close to −1.5 V vs. SCE but only if both tin and gallium were present; alloys containing only tin or only gallium did not dissolve until potentials positive to −0.7 V. Three alloys from different sources but containing similar amounts of Sn and Ga gave very similar electrochemistry although different stabilities to open circuit corrosion; the three alloys were characterised by SEM and TEM and differed in the size of the tin inclusions and aluminium grains. It was shown that the anodic dissolution of the aluminium around these inclusions to form rounded pits, quite different to the crystallographic pits observed with pure aluminium and other alloys, e.g. that containing Sn but not Ga. The distribution of the gallium in the alloy could not be defined but its critical role in allowing high rate dissolution at low overpotentials suggests that it is also located at or adjacent to the tin inclusions. Both the marked decrease in overpotential (∼800 mV) and the change in the appearance of the pits suggest that the presence of Sn and Ga in the alloy leads to dissolution by a different mechanism to that operating with pure Al.

While Al/air batteries with NaCl electrolytes have been developed [2–5], papers discussing the anodic dissolution reactions of appropriate aluminium alloys in this medium are relatively scarce [6–10]. The conclusions of our earlier study [1] were, however, entirely consistent with the data reported. Much more detailed studies of the dissolution of the Al alloys are available in alkaline electrolytes but the systems are quite different in the two electrolytes (i) the equilibrium potentials of the Al/Al(III) couples are estimated as −1.66 V in neutral media and −2.33 V in alkaline solution [11]; (ii) the corrosion potentials are quite different and follow this trend [3]; (iii) the product in alkaline media is the soluble species $Al(OH)_4^-$ but in chloride media largely ill defined insoluble species are formed [7,12]; (iv) on open circuit, H_2 evolution is rapid in alkaline media but difficult to observe in neutral chloride media [1,10,13]; (v) even high purity Al corrodes and dissolves anodically in alkaline media but in brine solutions, only some alloys dissolve anodically [1,3,5,6]; (vi) in brine media, corrosion occurs at specific sites whereas general corrosion occurs in alkaline media; (vii) in brine, the alloying elements are essential for rapid anodic dissolution while in alkaline media the main role of the alloying elements appears to be in minimising the parallel H_2 evolution. The mechanisms are clearly different.

In this paper, we now extend the study of the Al alloys containing both Sn and Ga in NaCl media using optical imaging with a high-speed camera. The studies used microelectrodes so that all of the electrode surface could be observed by SEM and EDX before and after the electrochemical experiments; in addition, the low electrode area ensured that only a small number of active sites are formed during dissolution. The application of optical imaging to the study of the corrosion and anodic dissolution of aluminium alloys is not new, but in general the papers in the literature achieve a lower resolution [9,14–16].

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doi:10.1016/j.electacta.2009.06.057

2. Experimental

2.1. Alloys and chemicals

Two alloys were studied. AB50V was a preferred alloy at the end of an Alcan programme in the 1980s and was a gift from Clive Tuck. The alloying elements were 0.6 wt% Mg, 0.1 wt% Sn and 0.05 wt% Ga. I0 was prepared by Innoval Ltd. and had the added elements 0.4 wt% Mg, 0.07 wt% Sn and 0.05 wt% Ga. Despite some differences in structure probably due to differences in heat regimes and mechanical working during fabrication [1], their electrochemistry was very similar and they were used interchangeably during these experiments. The electrolyte was prepared using deionised water from a Whatman Analyst purification system and Analytical Grade sodium chloride from Fisher Scientific. All experiments were carried out at room temperature, 290 ± 3 K.

2.2. Electrochemical cells and instrumentation

All electrochemical experiments were carried out in three electrode glass cells with a Pt counter electrode and a saturated calomel reference electrode. The reference electrode was placed as close as possible to the surface of the working electrode. In experiments employing the high-speed camera, the cell had a flat optical window and the working electrode was placed ~2 mm from this window. The working electrodes were fabricated by cutting a sample of the alloys to a point and then sealing in a slow-setting epoxy resin (Stuers, Epofix). The epoxy resin set electrode was then only lightly ground and polished, as follows: (i) mechanically ground with 1200 grade emery paper for 1 min; (ii) mechanically polished with 1 μm diamond paste on a DP-mol cloth for 3 min. Between each stage, the surface was washed with soap solution and then rinsed thoroughly with water before being dried. The preparation of aluminium surfaces for high resolution electron microscopy has been described previously [1].

The voltammetry and chronopotentiometry experiments were controlled with an EG & G model 273 Potentiostat run by Powersuite software. Open circuit potentials were measured with a Fluke 83 Multimeter.

High resolution electron microscopy used a Jeol JSM 5910 fitted with an Oxford Inca 300 EDX was used for detailed surface characterisation. The electron microscopy carried out in conjunction with the optical microscopy employed an environmental scanning electron microscope, a Philips XL30 ESEM fitted with an EDAX International Phoenix 2 EDX, available on demand in the laboratory. The use of this instrument together with the impossibility to prepare the surface during the experimental procedure made the detection of tin inclusions less certain.

2.3. High resolution imaging

A Photron APX-RS high-speed camera fitted with a Navitar 12X lens and a 2X extension tube and 2× lens adaptor was employed to image the surface of the electrode at a variety of frame rates. The camera had solid state memory (6 Gb) which allows considerable time periods (e.g. ~240 s at 50 frames/s and 768 × 672 pixels) to be acquired. The data was then transferred to a PC through a firewire connection. These images were then processed/analysed to characterise processes occurring at the electrode surface. Often the most convincing presentation, not possible in a paper, was to combine the frames into a video. Lighting of the sample was critical and a 150 W cold light source proved adequate (SCHOTT–KL 1500).

The equipment employed allows the identification and monitoring of features 10–20 μm in size. The image of the surface seen results largely from shadowing and therefore on the direction of the illumination. It takes time (up to 30 min) to set up the lighting and focus the camera after the cell has been filled with electrolyte. It therefore looks at the surface after this period. The need to place the electrode surface close to the optical flat also sometimes leads to the trapping of gas bubbles.

3. Results

The size and distribution of tin inclusions in the alloys were determined by high resolution SEM of well polished samples using the BEC detector of the Jeol JSM 5910 scanning electron microscope (e.g. see Fig. 6 in [1]). The tin inclusions are clearly seen as white spots and their identity could be confirmed by EDX analysis. With both alloys, I0 and AB50V, the tin inclusions are randomly distributed over the surface. The alloy I0 has inclusions with dimensions 1–8 μm and a number density of ~20 per mm^2 while the alloy AB50V had much smaller inclusions, mostly ~1 μm with a much higher number density, ~250 per mm^2.

3.1. Experiments on open circuit

In the initial experiments with the camera system, the surface of the alloy, I0, was observed at open circuit in 2 M aqueous sodium chloride. The samples were prepared as microelectrodes, with areas typically ~0.1 mm^2, in epoxy resin surrounds so that the whole sample could be monitored and that they would contain only a small number of tin inclusions. Because of the small size of the electrodes and the structure of the electrode support, they could not be as well polished as the samples used in the surface characterisation studies [1]. It was also recognised that the sample would be in the electrolyte for a significant period while the camera was set up and focused before an experiment could be commenced; in fact, this period was typically up to 30 min and changes to the surface during this period are inevitable. Fig. 1 illustrates the experimental sequence. Fig. 1(a) shows a SEM image immediately before immersion of the sample into the 2 M NaCl; there are no features visible on this scale and a single tin inclusion could be located as indicated by the white circle. Fig. 1(b) shows an image taken with the camera of the surface before immersion and there are still no clear features on the surface. After immersion in 2 M NaCl, H_2 gas bubbles were seen to grow very slowly at three specific points on the surface including the tin inclusion identified by the ESEM, see Fig. 1(c). After a period of some 30 min, the gas bubbles were removed and pits, visible as white areas (emphasised with dashed, white circles) because of the non-conducting product of corrosion, could be observed at the sites of the hydrogen bubbles, Fig. 1(d). Unfortunately, the technique does not give detailed information about the structure of the pits or the morphology of deposits within the pit but such information is readily obtained by SEM [1].

Fig. 2 reports a similar experiment with the other alloy, AB50V, with a similar elemental composition. With this sample, two inclusions were identified, see Fig. 2(a). After immersion in the 2 M NaCl, hydrogen bubbles were observed at the sites of both tin inclusions, Fig. 2(c), with pits observed after the removal of the gas bubbles, Fig. 2(d).

The rate of H_2 is, however, very slow and hence these conclusions drawn with the aid of the camera are not inconsistent with the corrosion tests reported earlier [1] where the observation was only by eye. In chemical etching and anodic dissolution of the alloys, it was also found that pit formation is generally associated with a tin inclusion [1]. The limitation in these experiments is identifying all the tin inclusions with the procedures used. The experiments with the camera, however, clearly establish that hydrogen evolution is directly associated with pit growth. It also seems reasonable to conclude that since tin is a much better catalyst for H_2 evolution than aluminium, the tin inclusions are acting as cathodic centres and