Electrochemistry Communications 81 (2017) 84–87

Contents lists available at ScienceDirect

Electrochemistry Communications

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

Droplet cell investigation of intergranular corrosion on AA2024

Remy Bonzom, Roland Oltra*

ICB, UMR 6303 CNRS Université de Bourgogne Franche Comté, Dijon, France

ARTICLE INFO

Keywords:
Intergranular corrosion
Aluminium alloy
Droplet cell
Anodic current
Foil penetration technique

ABSTRACT

An original method combining a droplet cell with direct optical interrogation of the reverse side of a 50 μm thick foil AA2024 has been tested to evaluate the possible analysis of the current during intergranular corrosion tests. The foil microstructure and the selected orientation were suitable for recording the current generated during the propagation in volume of a well-defined grain boundary trace. Even if it is impossible to reach a charge and mass balance from these preliminary attempts, it was demonstrated that it is possible, despite hydrogen evolution, to record a current transient resulting from the full penetration of an intergranular path.

1. Introduction

This work is related to intergranular corrosion (IGC) on Al–Cu alloys which is known to be controlled by preferential anodic dissolution of the Cu-depleted zone caused by structural hardening treatments [1]. These thermal treatments induce intermetallic (IM) phase precipitation (Al_2Cu, Al_2CuMg) inside the alloy and especially along the grain boundaries. The dissolution process mainly affects the active anodic head at the tip of the grain boundary and to a lesser extent the faces of the surface of the grain ‘crevice’ behind the active anodic head [2]. It could therefore be assumed that a measure of the anodic part of the total current during potentiostatic experiments would be useful to establish the charge and mass balance in order to evaluate the IGC propagation rate.

In fact, current analysis is not widely used in IGC studies and physical methods such as the foil penetration technique have been preferred to examine the IGC propagation rate [3,4]. This technique makes it possible to detect the arrival of the first full penetrating intergranular (IG) path from a physical measurement on the opposite side of a thin foil.

Nevertheless, Rota and Böhni [4] tried to analyze the recorded current during foil penetration experiments in a short transverse direction on a fine-grained commercial 2024 alloy. The current–time variation was discussed qualitatively and supported by observations of metallographic cross-sections. Correlation of the current–time curves and the attack morphologies (after penetration) shows three stages of subsequent IG attack. During the activation stage, the current increases because the number of active sites is increasing. Then there is a transition stage, characterized by a small decrease in the total current, corresponding to propagation in volume to all the grain boundaries. Finally, the current reaches a stable regime which is related to macroscopic grain dissolution.

However, it is impossible to relate the total charge to the dissolution process of the Cu-depleted zone at the head of the grain boundaries due to the uncontrolled number of active sites convoluted by the number of ramifications. For other reasons, such as the stochastic nature of corrosion processes, similar conclusions can be drawn for other forms of localized corrosion. To improve the analysis of the current generated by a local corrosion site, a number of local probe techniques have been developed.

One of the methods commonly used to study pitting on inclusions on stainless steels [5] and trenching around IM phases on Al alloys [6] is the micro-capillary electrochemical cell technique. It has been suggested that this technique [7] may be useful for studying IGC initiation at a micrometer scale. The idea is to stick a glass capillary above the grain boundary or above the interior of the grain. To our knowledge only unpublished results [8] describe the use of a micro-capillary electrochemical cell to record locally the polarization curve of the surface along a grain boundary and inside the matrix. It was shown that it is possible to measure the electrochemical characteristics of grain interiors and grain margins separately.

At the same spatial resolution scale as grain boundaries, a micro-capillary electrochemical cell has been used to study the interfacial properties of an inclusion embedded in a stainless steel matrix [9]. In this quasi-unique study, local potentiodynamic polarization curves were measured at different spots spaced 5 μm apart through the interface between a MnS inclusion and the surrounding matrix using a glass micro-capillary with a tip diameter of about 2.5 μm.

In this paper, we report how it is possible, with a local electrochemical probe including a well-designed capillary, to record the

---

[*] Corresponding author.
E-mail address: roland.oltra@u-bourgogne.fr (R. Oltra).

http://dx.doi.org/10.1016/j.elecom.2017.06.011
Received 15 May 2017; Received in revised form 2 June 2017; Accepted 9 June 2017

current transient corresponding to a well-controlled propagation occurring in the volume along a selected grain boundary face. In the long term, this work is expected to improve our understanding of the relation between the current–time variation and the propagation rate.

2. Experimental

In a preliminary part of this work, we tried to use the micro-capillary electrochemical cell technique mentioned above to study the propagation of IGC on AA2024. However, it was impossible to maintain the polarization of the sample for more than a few seconds due to the formation of hydrogen bubbles at the tip of the capillary which induced breakdown of the electrical circuit.

Instead, a droplet cell composed of a PTFE® capillary with an internal diameter of 500 μm was used to study the local electrochemical response during a corrosion test on AA2024 thin foil. The PTFE® capillary is designed with a geometry (open cone) which is more suitable to the release of evolved gases (Fig. 1b). This droplet cell is based on a commercial SDC (Scanning Droplet Cell from Sensolytics GmbH) and can be moved by stepper motors (Fig. 1a). A miniaturized reference electrode and a Pt counter electrode are housed in the head. Reproducible droplet formation is controlled by a micro-metering pump. To prevent leakage, the PTFE® capillary was moved towards the substrate until the force reached 200 mN (the force was controlled by a sensor integrated in the Sensolytics device).

The experiments were performed on a 50 μm thick foil which was obtained by mechanical polishing of a 200 μm thick foil. Foils of thickness 200 μm were machined from thick plates of AA 2024-T351 (wt%: Cu 4.50%, Mg 1.44%, Mn 0.60%, Si 0.06%, Fe 0.13%, Zn 0.02%, and Ti 0.03%). The exposed face (longitudinal (L)-short transverse (ST)) had previously been mechanically ground in ethanol with silicon carbide papers up to 2400 grit and had been finished by a 3 μm polishing step. The microstructure of this foil exhibits the following average grain sizes: 700 μm in L (longitudinal), 300 μm in LT (long transverse) and 100 μm in ST (short transverse) directions. There is no opportunity to observe branching at a long distance (following a "brick-wall" feature). It can be reasonably assumed that a single grain boundary will be involved because the thickness of the foil is 6 times lower than the average grain size in the LT direction. However, a discontinuity in the IG path involving two consecutive grains cannot be excluded (as shown in Fig. 1a).

Potentiostatic tests were performed in a 0.1 M NaCl solution at a potential of −560 mV (SCE), which is only 20 mV higher than the breakdown potential (−580 mV (SCE)) and consequently makes it possible to activate a reduced number of grain boundary traces on the 0.2 mm^2 exposed surface (Fig. 1c). The sample was in contact with the solution for 2 min prior to the start of the potentiostatic measurement. It is important to bear this in mind as it induces dealloying of coarse IM particles, as discussed in the next section. Simultaneously, the end of the full penetration of the activated grain boundary trace (Fig. 1c) is detected by continuous optical interrogation of the reverse side of the foil (Fig. 1a) [10].

3. Experimental results

The results of the corrosion test are summarised in Fig. 2. There is a first step of 230 s during which a cathodic current is measured. The dealloying of IM coarse particles takes place during this OCP step and it is likely that this cathodic current is induced by the oxygen reduction reaction (ORR) on Cu-rich remnants of the IM coarse particles. Indeed, Boag et al. [11] have shown that S-phases undergo complete dealloying in the first five minutes after immersion in chloride-containing solutions. Step I can be considered to be the incubation step because the ORR on Cu-rich remnants of IM coarse particles has been clearly demonstrated to be the main controlling process [12] at the initiation sites for IGC.

Then the current increases and reaches a maximum at around 570 s (end of step II). Next, the current begins to decrease and an electrolyte leakage simultaneously occurs on the opposite side of the foil. This leakage occurs along a linear trace (see diagram B in Fig. 2) following the foil microstructure and is clearly related to a grain boundary penetration. After this observation, the current continues to decrease and the linear trace expands on the reverse side of the foil until it stops growing at 700 s (end of step III and diagram C). A disconnected second trace simultaneously occurs on the reverse side of the sample. Because no second trace was observed on the exposed surface this probably corresponds to a typical discontinuity in the IG path involving the assembly of two consecutive grains (see schematic diagram of the specimen in Fig. 1a). This is followed by a large purge of the electrolyte trapped in the dissolved grain boundary (diagram D). The pH value of this purged electrolyte was measured to be around 1 in other foil penetration experiments conducted at a larger scale [13], and this explains why the total current, which will then also include the current resulting from the corrosion of the wetted parts of the reverse side, can

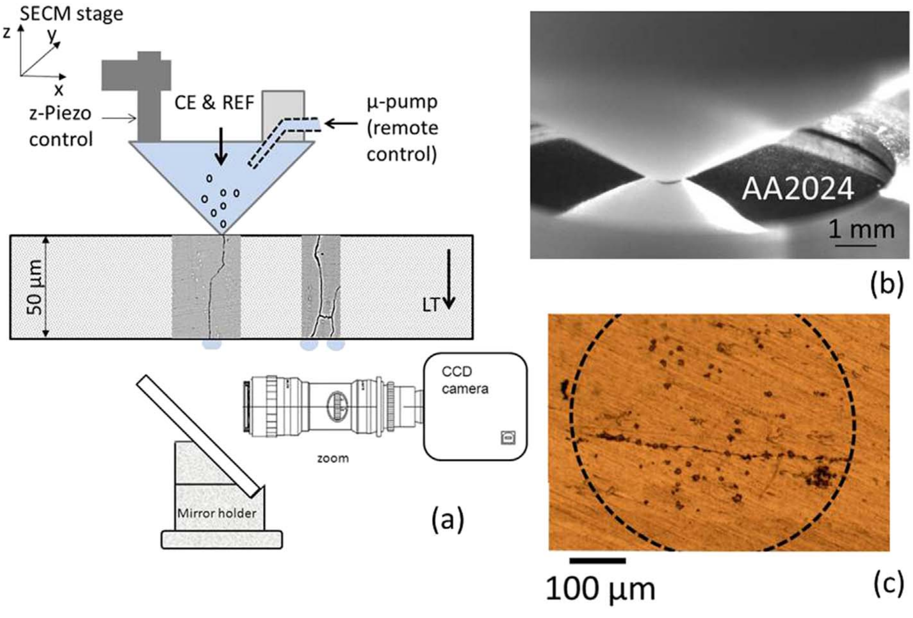

Fig. 1. Local electrochemical monitoring of intergranular corrosion.
(a) Schematic diagram of the experimental set-up. The droplet cell is attached to a piezoelectric arm fixed on a x–y–z positioner stage of a Scanning Electrochemical Microscope (SECM). The end of the full penetration of the activated grain boundary trace (c) is detected by continuous optical interrogation of the reverse side (see ref. [10]). The most likely situation corresponds to direct propagation but a discontinuity in the IG path involving the assembly of two consecutive grains cannot be excluded, as shown on the right of the cross-section of the schematic specimen.
(b) Macroscopic view of the upper face showing the close contact between the PTFE capillary of the droplet cell with the AA2024 foil surface.
(c) Top view of the working electrode area (dashed circle) after the corrosion test. A linear trace of an attacked grain boundary can be clearly seen.