Corrosion of 2024 Aluminium Alloy in Restricted Volumes of Electrolyte: Use of a Thin Layer Cell

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Introduction

Corrosion in confined media is encountered in many fields of application, such as atmospheric corrosion, crevice, pitting, occluded cells beneath a deposit etc… However, even if it was widely reported that the results classically obtained in bulk conditions (infinite electrolyte volume) do not necessarily remain valid in thin electrolyte films [1, 2], the precise influence of confinement on corrosion processes still remains poorly understood.

For the 2024 aluminium alloys, the presence of copper rich particles embedded in a matrix of aluminium, leads to localized attack as a result of galvanic coupling. The formation of a crevice between Al and the particles is well understood and is attributed to anodic dissolution of aluminium. More surprising is copper re-deposition which is often observed in the vicinity of the crevice. In a recent work [3], using model couples made of pure copper and pure aluminium, copper replating at the Al/Cu interface has been correlated with the presence of a confined medium between the two metals. Thus in the present work, a thin-layer electrochemical cell was used in order to reproduce the experimental conditions close to that encountered in a crevice. A simple system consisting of a pure aluminium sheet facing a pure copper sheet is used, in the presence of 0.1 M Na_2SO_4 solutions.

Experimental

The electrochemical thin-layer cell is reported in Fig.1. It allows confinement of an electrolyte layer (down to 50 μm thickness) between two parallel plans containing respectively a pure copper and a pure aluminium surface. The two metals are the cross sections of metallic cylinders, with diameter of 30 mm and are sealed in a cylindrical epoxy resin insulating holder. Prior to use, the two electrodes were mechanically polished with silicon carbide papers (up to 4000 grade), ultrasonically cleaned with distilled water and dried with a N_2 flux. The lower electrode (copper) was embedded in the bottom of a perforated glass cell, filled with a 0.1 mol L^{-1} air-saturated Na_2SO_4 solution. Facing the lower electrode, a mobile upper electrode (aluminium), was moved downwards in order to ensure the confinement of the electrolyte between the two metallic surfaces. The two metals electrically connected constituted the working electrode. A saturated mercury sulphate electrode (SSE; +0.645V/SHE) used as the reference electrode and a large platinum grid used as the counter electrode were located outside the confined zone. The equipment for electrochemical measurements is an Ameteck (EGG Princeton Applied Research) The samples were observed after several days of polarisation using two scanning electron microscopes a Leica Stereoscan 440 and a MEB-FEG Zeiss Ultra 55 equipped with a quantitative energy dispersive X-ray spectrometer (EDS) for performing mapping images.

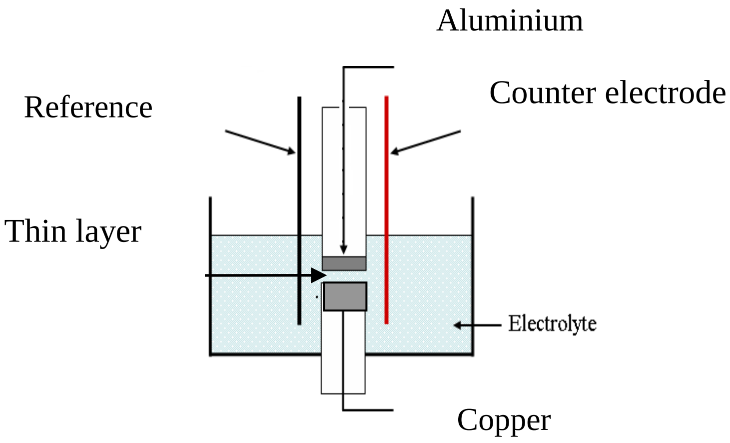

Fig 1-Schematic representation of the thin layer cell

Results and discussion

Model electrodes made of pure aluminium coupled with pure copper have be used in the thin-layer cell as described in Fig.1. As an example, for a 150 μm thick electrolyte layer between copper and aluminium, the galvanic potential and current were followed as a function of time (Fig. 2a and b)

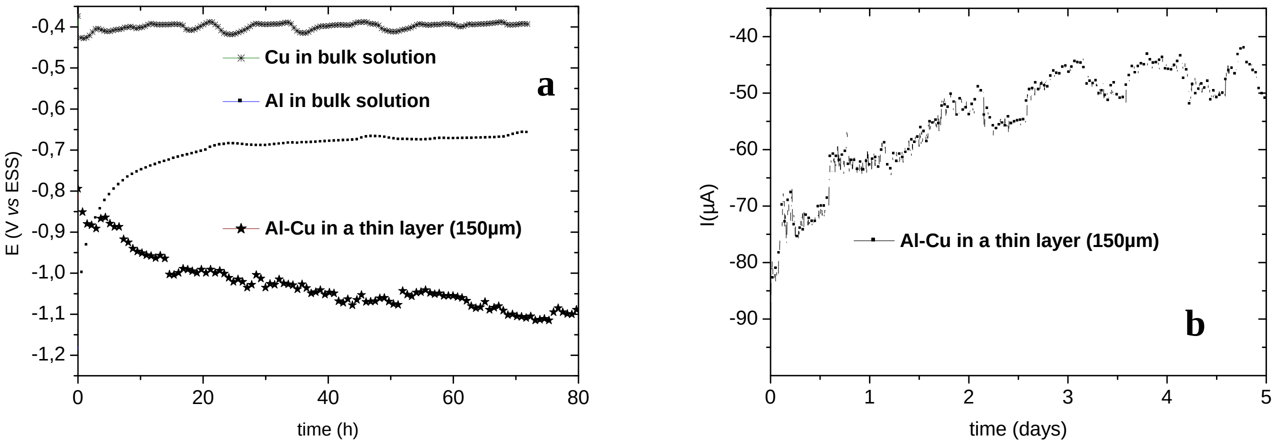

Fig 2 – a)- Comparison between the open-circuit potentials for the pure metals in a bulk solution, and the galvanic potential for Al-Cu coupled samples in a thin layer electrolyte (0.1M Na_2SO_4),
b) - evolution of the galvanic current as a function of time (S = 7 cm^2 for the two metals)

After 5 days of coupling, the galvanic potential was about -1.1V/SSE and the galvanic current was close to 7 μA /cm^2. A white gelatinous layer characteristic of aluminium hydroxide was present in the thin layer and at the surface of the aluminium electrode. Mapping images were performed at the aluminium electrode in order to detect eventual copper deposition.

Copper islands are observed (Fig.3), but mainly at the edge and the wall side of the Al electrode. This indicates that copper dissolution during coupling between copper and aluminium is favoured in a zone close to the confined medium.

The presence of the white aluminium hydroxide layer in the thin layer indicates significant enrichment in aluminium ions in the confined zone, and simultaneously significant acidification of the medium due to Al^{3+} hydrolysis according to:

$$Al(H_2O)_6^{3+} + SO_4^{2-} \leftrightarrow Al(OH)(SO_4)(H_2O)_4 + H^+ + H_2O$$

pH measurements performed in the thin layer showed that values close to 3.5 can be reached after a few hours of immersion.

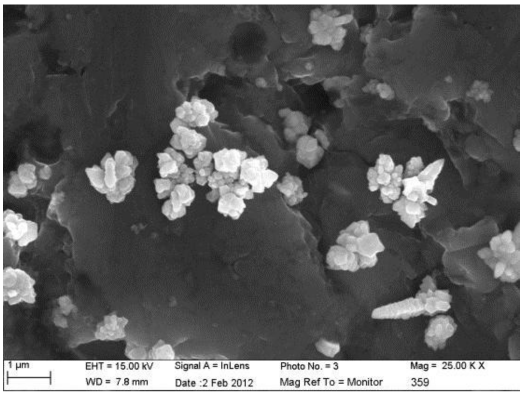

Fig 3- SEM image of copper crystals replated on the surface of aluminium in a thin-layer cell

Conclusion

Anomalous copper dissolution at potentials more negative than the equilibrium potentials for Cu^{2+}/Cu or Cu^{+}/Cu are shown to be correlated with the formation of confined regions between aluminium and copper. The confinement allows the solution to be enriched with aluminium ions and simultaneously to reach more acidic pH values during aluminium dissolution.

Evolution of local pH from acidic values in the crevice (due to aluminium dissolution) towards more alkaline values (due to O_2 reduction) at the mouth of the crevice where cuprous oxide is formed was taken into account to explain anomalous copper dissolution. An overall mechanism is suggested involving cuprous oxide formation followed by dissolution and replating onto the aluminium sheet.

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