



HAL
open science

Anomalous Dissolution of Copper in Al-Cu alloys

Eliane M M Sutter, Samir Joma, Thi Tuyet Mai Tran, Mamie Sancy, Bernard Tribollet

► **To cite this version:**

Eliane M M Sutter, Samir Joma, Thi Tuyet Mai Tran, Mamie Sancy, Bernard Tribollet. Anomalous Dissolution of Copper in Al-Cu alloys. 6th International Symposium on Aluminium Surface Science and Technology (ASST 2012), May 2012, Sorrente, Italy. Paper 1. hal-04114171

HAL Id: hal-04114171

<https://hal.science/hal-04114171>

Submitted on 1 Jun 2023

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Anomalous Dissolution of Copper in Al-Cu alloys

**E.M.M. Sutter^{1,2}, S. Joma^{1,2}, T.T.M. Tran^{1,2}, M. Sancy^{1,2,3}
B. Tribollet^{1,2}**

¹CNRS, UPR15, Laboratoire Interfaces et Systèmes Electrochimiques, F-75005 Paris, France,

²UPMC Univ Paris 06, UPR15, LISE, 4 place Jussieu, F-75005 Paris, France

³Academia Politécnica, Fuerza Aérea de Chile, J.Miguel.Carrera 11087, Santiago, Chile

E-mail: eliane.sutter@upmc.fr.

Abstract:

During galvanic coupling between copper and aluminium, copper can undergo anomalous dissolution and replating onto the surface of aluminium. This observation has often been made on 2024–T3 alloys at a micrometric scale, at the interface between the aluminium-rich matrix and the intermetallic particles, as well as at a more macroscopic scale, in the vicinity of the interface between a 2024 sheet and a rivet with similar composition. The aim of this work is to show that anomalous copper dissolution has to be correlated with the presence of a confined medium, rather than with galvanic coupling. A confined medium was simulated using a thin-layer electrochemical cell and copper replating at the mouth of the crevice was followed using EDS analysis. A mechanism is suggested involving local acidification in the crevice, due to Al dissolution. Furthermore pH variations between the inner acidic zone and the more alkaline zone at the mouth of the crevice have also to be taken into account.

Keywords: Al-Cu alloys, thin-layer cell, galvanic coupling

1. Introduction

In the 2024 alloy, which is a widely used alloy in the aeronautic industry, different types of corrosion can be observed. First of all galvanic corrosion is often reported and is due to the presence of copper rich particles, embedded in a matrix of aluminium leading to localized attack. Corrosion is also sometimes observed when two 2024 sheets are connected with a rivet. Since rivets are generally made of a slightly different alloy than that of the plates, corrosion is usually described as galvanic corrosion. In a recent work, an aluminium-copper couple was considered for modelling galvanic coupling between these two metals [1]. It was shown that the corrosion phenomena mainly occurred at the Al/Cu interface, according to a three-step mechanism: the local cathodic current due to the oxygen reduction on copper significantly increased near the Al/Cu interface and led, as a consequence, to a local pH increase. This high local pH induced local aluminium dissolution and then a deep crevice was formed at the interface between aluminium and copper. Experimentally a copper deposit, located on the aluminium material, was observed near the Al/Cu interface, indicating that copper dissolution must be taken into account.

Thus the aim of this work is to highlight the mechanism of copper dissolution and deposition at the aluminium matrix and to

analyse the influence of confinement on this behaviour, using different set-ups. In the first part of this work, two systems consisting of a AA2024 sheet / AA20470 rivet on one hand and of a AA2024 sheet / AA2024 rivet on the other hand are considered after immersion during several hours in a 0.1M Na₂SO₄ solution. Particular attention is paid to the interface between the sheet and the rivet using an optical and a scanning electron microscope. The comparison between the behaviours of the two systems will allow to conclude, if the corrosion is due to galvanic coupling or to the presence of a crevice between the sheet and the rivet.

In the second part of this work, a thin-layer electrochemical cell [2] is used to reproduce the experimental conditions close to that encountered in a crevice, since the chemical composition of the thin electrolyte layer is expected to drastically change during the immersion. In this part a simple system consisting of a pure aluminium sheet facing a pure copper sheet is used in the presence of 0.1 or 0.01 M Na₂SO₄ solutions.

2. Experimental

The electrochemical thin-layer cell was described in details elsewhere [2] (schematic 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 (both 99.9% weight from Goodfellow). 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; $+0.645\text{V}/\text{SHE}$) 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 Ametek (EGG Princeton Applied Research) potentiostat/galvanostat model 263A monitored by a personal computer using Zware softwares). 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.

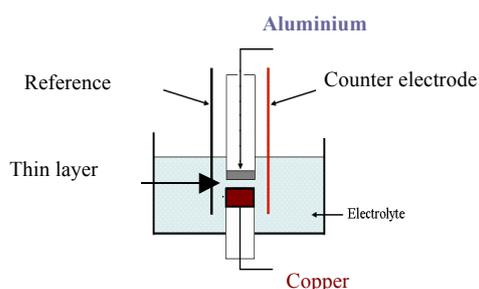


Fig 1-Schematic representation of the thin layer cell

The chemical composition of the alloys used for sheet/riquet assemblies are given in Table 1

Alloy	Al/wt.%	Cu/wt.%	Zn/wt.%	Mg/wt.%	Fe/wt.%
2024	94,20	4,04	-	1,48	-
20470	92,23	0,68	-	0,37	1,67

Table 1: Composition of the alloys used in this work

For the experiments performed on pre-oxidized copper electrodes, an oxide layer was previously formed in an air-saturated $0.01 \text{ M Na}_2\text{SO}_4$ solution through polarisation of the copper electrode at $-0.2\text{V}/\text{SSE}$ during 30 min. The thickness of the oxide layer was estimated by coulometry to be about $300 - 400 \text{ nm}$

3. Results

3.1 Assembling of an AA 2024 sheet with an AA 20470 rivet.

The rivet was introduced by force in a sheet, providing zones with joined interfaces and some zones with an interstice of a few μm thickness between the two alloys (Fig 2 a). After immersion in an air saturated $0.1\text{M Na}_2\text{SO}_4$ solution during 12 days, the interfaces were analyzed using SEM microscopy (Fig 2b). The images showed that the corrosion processes mainly affect the interface, where a crevice was initially present between the sheet and the rivet, or a zone close to this interface.

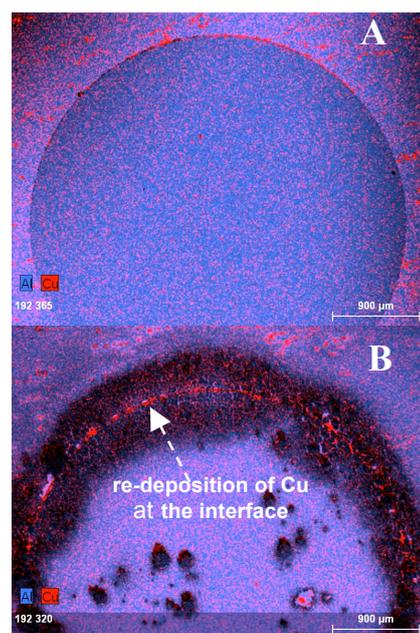


Fig 2 - Assembly between a 2024 sheet and a 20470 rivet A) -before exposure, B) -after 12 days of exposure to a $0.1\text{M Na}_2\text{SO}_4$ solution, (Cu is in red, Al in blue).

To check if this type of damage is due to galvanic coupling between two alloys with slightly different composition (see table 1), a similar assembly was performed but using alloys with same compositions.

3.2 Assembling of an AA 2024 sheet with an AA 2024 rivet.

Surprisingly, the behaviour of the assembly after a few days of immersion in a 0.1M Na_2SO_4 solution is very similar to that described in §3.1, with important corrosion damages localised at the interface between the sheet and the rivet, mainly near the zones where interstices were present before immersion.

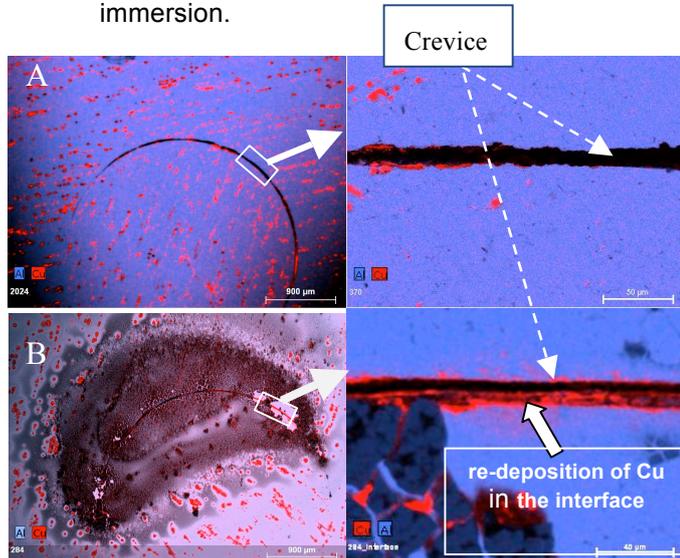


Fig 3 - Mapping image of an assembly between a 2024 sheet and a 2024 rivet A) -before exposure B) -after 12 days of exposure to a 0.1M Na_2SO_4 solution, with enlargement of the zone at the right (Cu is in red, Al in blue).

Figure 3 is a mapping image of the interface showing the repartition of Al and Cu in the assembly and an enlargement of this zone is presented at the right. The red spots in the matrix are due to the copper-rich intermetallics (IMP) present in the AA 2024 alloy. But the noticeable result here is the enrichment in copper in the vicinity of the interstice between the sheet and the rivet. These qualitative experiments clearly demonstrate that the damages observed in the two types of assemblies must be attributed to the presence of a confined zone between the sheet and the rivet and not to galvanic coupling. Another interesting point is the copper redistribution along the interstice onto the surface of the sheet (Figure 3B at the right), which involves previous copper dissolution during the corrosion process. Such behaviour is very similar to anomalous dissolution of copper, which has been reported in previous works for AA 2024 alloys [3-6].

3.3 Simulation of copper dissolution/replating during galvanic coupling between copper and aluminium in a thin-layer cell.

To understand the corrosion behaviour of copper-rich aluminium alloys, model electrodes made of pure aluminium coupled with pure copper have been used and the thin-layer cell described in Fig.1 allowed to reproduce the confined electrolyte between the two metals. 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. 4a and b)

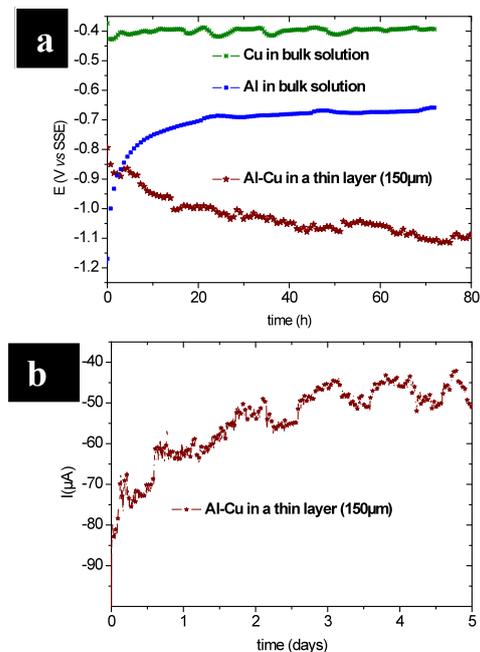


Fig 4 – a)- Comparison between the open-circuit potentials for the pure metals in a bulk solution, and the galvanic potential for Al-Cu coupled samples in a thin layer electrolyte (0.1M Na_2SO_4), b) - evolution of the galvanic current as a function of time ($s = 7 \text{ cm}^2$ for the two metals)

After 5 days of coupling, the galvanic potential was about -1.1V/SSE and the galvanic current was close to $7 \mu\text{A} / \text{cm}^2$. 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. Mapping images from the centre and from the edge of the aluminium electrode are reported in Figure 5.

Copper islands are observed 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:

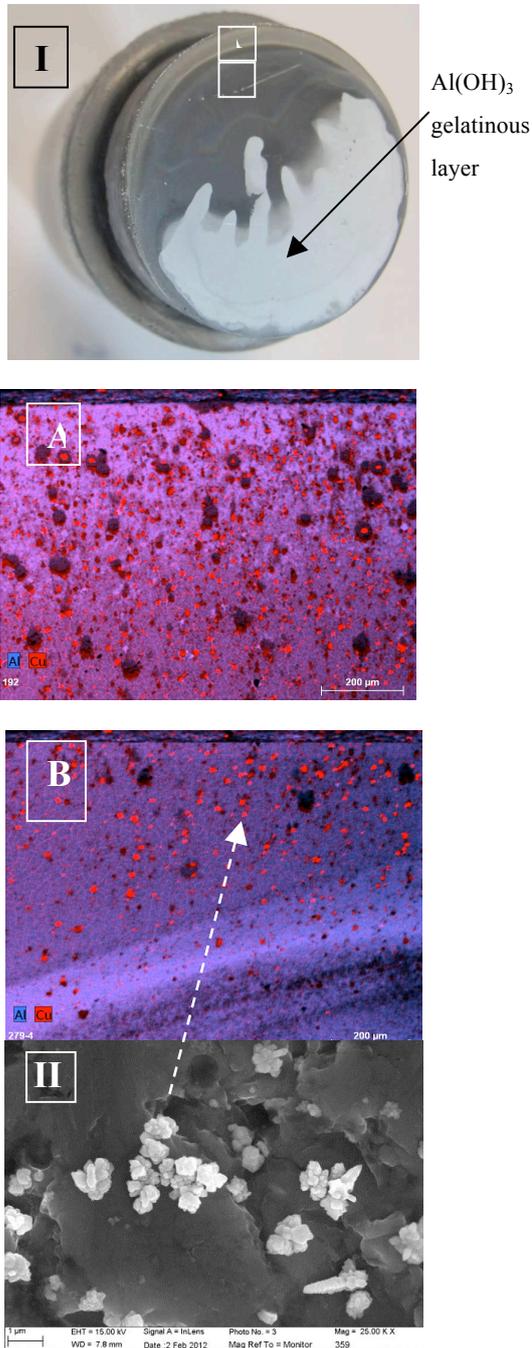


Fig 5 – I)-Optical observations of the surface of the aluminum disk electrode after coupling with copper in the thin layer cell (150 μm thickness) after 5 days of immersion in a 0.1 M Na_2SO_4 solution, A)- SEM image at the edge of the disk B)- SEM image at 1mm from the edge (Cu is in red, Al in blue), II)- SEM image of copper crystals replated on the surface of aluminum.

A rough estimate of the pH reached after 5 days in the thin layer can be made from the

corrosion rate of aluminium in a 0.1M Na_2SO_4 solution and values between 3.5 and 4 are expected.

Attempts were made to reproduce in a bulk solution the chemical composition of the thin electrolyte layer.

3.4. Behaviour of copper in a bulk solution containing Al^{3+} ions.

Electrochemical measurements were performed in a bulk electrolyte in the presence of $0.1 \text{ mol L}^{-1} \text{ Al}_2(\text{SO}_4)_3$ and compared to those performed in the absence of aluminium ions. Fig.6 displays the cathodic potentiodynamic curves obtained after 3 hours immersion of a copper electrode and performed starting from open-circuit potential. In the absence of Al^{3+} , a low cathodic current density in the potential range [-0.4 to -0.8V] is due to oxygen reduction at the surface of cuprous oxide Cu_2O . The cathodic peak at -0.95V /SSE is usually attributed to reduction of cuprous oxide layer [7]. It is followed by a current plateau due to the diffusion limited oxygen reduction between -1.4 to -1.1 V /SSE.

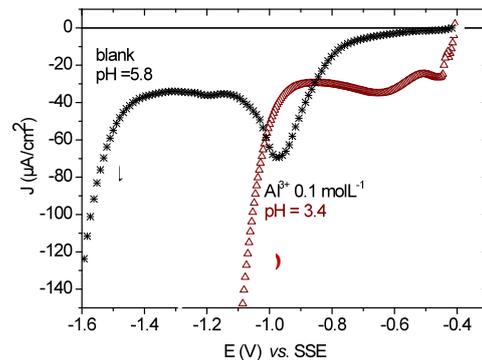


Fig 6- Cathodic behaviour of copper in a)- 0.1M Na_2SO_4 and b)- $[0.1\text{M } \text{Na}_2\text{SO}_4 + 0.1\text{M } \text{Al}_2(\text{SO}_4)_3]$ solution.

When aluminium ions are present in the solution, the open-circuit is slightly shifted towards more positive values (from -0.40 towards -0.38V). No cuprous oxide is present at the surface (absence of the Cu_2O reduction peak) and the diffusion current plateau due to oxygen reduction is reached in a potential range very close to the open-circuit potential.

From these results it clearly appears that acidification of the solution hinders cuprous oxide to form at the open-circuit potential before cathodic polarization. A hypothesis

could then be that cuprous oxide spontaneously formed at the contact of an aerated solution undergoes local dissolution at the mouth of the confined medium where acidification occurs. In order to gain further insight into the mechanism of anomalous copper dissolution, experiments were performed on pre-oxidized copper electrodes.

3.5. Corrosion of a pre-oxidized copper electrode in a thin-layer cell at pH 4.

Different assembling made of pre-oxidized copper electrodes facing an aluminium or a stainless steel electrode were compared in the thin-layer cell. The aim of using a stainless steel electrode instead of an aluminium one was to verify if copper dissolution in the thin-layer set-up is correlated with the presence of aluminium or if copper corrosion is only a result of the acidic pH in the confined medium.

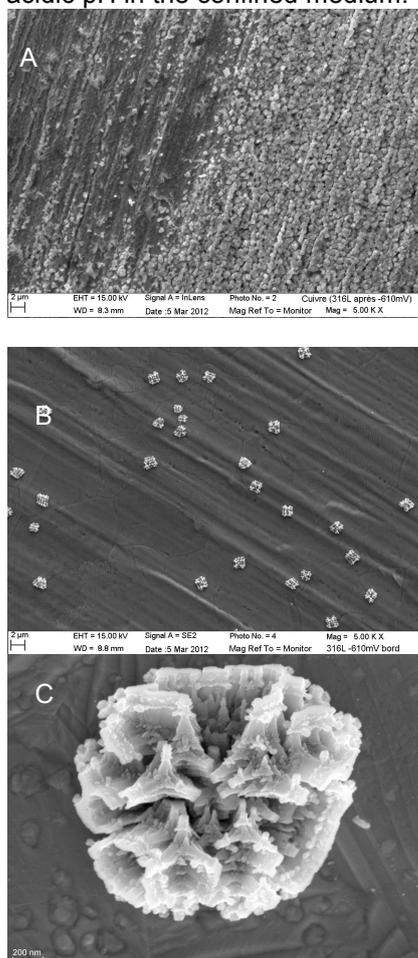


Fig 7 : SEM images, after 3 days of immersion in a 3 mm thick 0.01 M Na₂SO₄ solution, A)- the pre-oxidized copper at OCP -B) and C) the facing stainless steel electrode at -0.61 V/SSE.

As an example, Fig 7 shows a SEM picture of the surface of a stainless steel electrode which faced a pre-oxidized copper electrode, with an electrolyte layer of 3 mm between them. The solution was a 0.01M Na₂SO₄ solution acidified with sulphuric acid down to pH 4. The stainless steel was polarized at E=-0.61V /SSE, which is the usual open-circuit potential of AA 2024 alloy in an aqueous solution. After three days, the cuprous oxide was partially dissolved (Fig 7A) and the stainless steel electrode facing the copper electrode was clearly covered with 2 μm large copper crystals (Fig 7B and C).

4. Discussion

Previous observations clearly showed that anomalous copper dissolution at potentials more negative than the equilibrium potentials for Cu²⁺/Cu or Cu⁺/Cu has to be correlated with the formation of confined regions between aluminium and copper-rich intermetallic particles or in the presence of any crevice in assembling made of copper rich aluminium alloys. The confinement allows the solution to be enriched with aluminium ions and simultaneously to reach acidic pH values (between 3.5 and 4 after a few days) during aluminium dissolution.

The presence of cuprous oxide before the set up of the thin layer favours the dissolution / redeposition of copper at the surface of the facing electrode. In a crevice configuration we suggest that dissolution of copper occurs mainly at the mouth of the crevice where the reduction of oxygen leads to alcalinisation of the interface and consequently to stabilisation of oxide. Thus modification of local pH from alkaline (during O₂ reduction) towards more acidic pH at the mouth of the crevice or of the interstice between the IMP and the matrix could explain successive formation and dissolution of cuprous oxide.

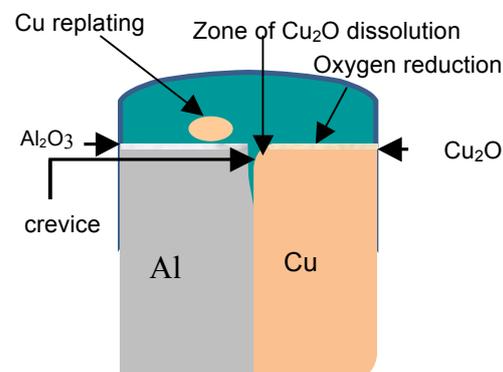


Fig 8 Schematic illustration of a mechanism for copper dissolution and replating.

The suggested mechanism for copper dissolution is the following (Fig. 8):

At the beginning of immersion, aluminium is in a passive state and a cuprous oxide layer is present at the copper surface in contact with the air-saturated electrolyte. Oxygen reduction occurs at the surface of the oxide, maintaining the interfacial pH in an alkaline range and consequently stabilizing the cuprous oxide.

Due to galvanic coupling with copper, dissolution of Al is favoured mainly at the interface between the two metals leading to crevice formation. Al^{3+} concentration increases in the crevice and the pH gets more acidic. Acidification of the solution at the edge of the crevice (due to protons diffusion from the crevice) is responsible for cuprous oxide chemical dissolution into cupric ions, which are further reduced at the surface of the aluminium matrix, in the vicinity of the crevice.

According to Fig 6, when cuprous oxide is dissolved, the rate of oxygen reduction at the metallic copper is enhanced (in comparison with the rate in the presence of Cu_2O), the pH is likely to increase again and cuprous oxide to be formed again. The periodic pH variation allows the overall mechanism to be repeated.

5. Conclusions

Anomalous copper dissolution at potentials more negative than the equilibrium potentials for Cu^{2+}/Cu or Cu^+/Cu were shown to be correlated with the formation of confined regions in two different situations: at a microscopic scale between aluminium and copper-rich intermetallic particles, and at a macroscopic scale at the interface between a 2024 sheet and a rivet. 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 should be taken into account to explain the anomalous dissolution of copper during galvanic coupling with aluminium. It is noticeable that for the same value of the potential, chemical dissolution and electrochemical replating of copper occur simultaneously, due to different pH values inside and outside the confined medium.

6. Acknowledgements

The authors thank Stephane Borensztajn and Françoise Pillier CNRS, UPR15 – LISE for SEM pictures and Axel Desnoyers de Marbaix for technical support.

7. References

- [1] J.B. Jorcin, C. Blanc, N. Pébère, B. Tribollet, V. Vivier, J. Electrochem.Soc. 155 (2008) C46.
- [2] E. Remita, E. Sutter, B. Tribollet, F. Ropital, X. Longuaygue, C. Travel-Condât, N. Desamais, Electrochim. Acta 52 (2007) 7715.
- [3] C. Blanc, N. Pébère, B. Tribollet, V. Vivier, Corros.Sci.52 (2010) 991.
- [4] M.B. Vukmirovic, N. Dimitrov, K. Sieradzki, J. Electrochem.Soc. 149 (2002) B428.
- [5] R.G. Buchheit, M.A. Martinez, L.P. Montes, J. Electrochem.Soc. 147 (2000) 119.
- [6] R.G. Buchheit, R.P. Grant, P.F. Hlava, B. McKenzie, G.L. Zender, J. Electrochem.Soc. 144 (1997) 2621.
- [7] E.M.M. Sutter, B. Millet, C. Fiaud, D. Lincot, J. Electroanal.Chem. 386 (1995) 101.