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Galvanic Coupling Between Pure Copper and Pure Aluminum
Experimental Approach and Mathematical Model

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The corrosion behavior of a pure aluminum/pure copper couple in a weakly conductive sulfate solution was investigated. Potential and current distributions on the surface of the model couple at the beginning of immersion were obtained by solving the Laplace equation using a finite element method (FEM) algorithm. The potential distribution predicted by the calculations was checked using a Ag/AgCl microreference electrode. A good agreement was found between experimental and theoretical results. It was shown that the reaction occurring at the copper electrode was oxygen reduction, while aluminum remote from the Al/Cu interface remained in the passive state. Moreover, calculations predicted a large cathodic current, related to an increase in oxygen reduction, restricted to copper at the Al/Cu interface. This led to a local pH increase reaching values higher than 9, allowing the dissolution of aluminum to occur close to the interface. Combining these data with optical and scanning electron microscope observations after 24 h of immersion in the sodium sulfate solution allowed a three-step mechanism to be proposed to explain the corrosion damage, and particularly the presence of a copper deposit on the aluminum surface, some distance from the Al/Cu interface, a phenomenon currently observed in commercial copper-rich aluminum alloys.

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There is significant interest in the corrosion behavior of Cu-containing Al alloys, such as the 2024 aluminum alloy (AA2024), which remain of importance for aerospace applications due to their high strength-to-weight ratio. Consequently, the corrosion susceptibility of 2XXX Al-alloy series has been studied for a long time.1-12 The corrosion of AA2024 is mainly caused by the heterogeneous microstructure of the alloy, which has been intentionally developed to improve the mechanical properties of the material.

Among the different types of intermetallic particles present in AA2024 alloy, both coarse Al12CuMg particles, also called S-phase or Al–Cu–Mn–Fe particles (size: 1–30 μm) and smaller Al12CuMg particles (about 200 nm) present in the grain boundaries have been widely studied due to their reactivity that constitutes initiation sites to improve the mechanical properties of the material.13-23 Authors usually refer to a galvanic coupling phenomenon between the particles and the surrounding matrix. Zhu and Van Ooij24 showed that anodic Al12CuMg particles dealloyed both Al and Mg (with a more severe dealloying of the Mg) when immersed in a neutral 0.6 M sodium chloride solution. Simultaneously, a significant dissolution of the Al matrix surrounding the coarse particles was also observed. This mechanism is similar to that proposed by other authors.15,18,25 In previous studies, Blanc et al.12,14 discussed a slightly different mechanism, in which the copper-rich intermetallic reactivity was studied in a 0.1 M sulfate solution and described by a three-step process consisting of homogeneous dissolution of the particle, copper redeposition, followed by local dissolution of the matrix surrounding the particle. These phenomena have been widely investigated by electrochemical measurements in combination with scanning electron microscopy (SEM) and electron dispersive spectroscopy (EDS). However, conventional electrochemical methods lack spatial resolution, while microscopy techniques do not allow the in situ chemical composition to be determined; these are crucial for the understanding of the role of the intermetallic particles on the corrosion process. Consequently, many authors have used atomic force microscopy (AFM), which provides high lateral resolution to study dissolution phenomena occurring in the S-phase.18,23-27

To understand the corrosion behavior of copper-rich aluminum alloys, another alternative is to study the electrochemical behavior of model alloys that are representative of the different metallurgical phases.22,23 For example, thin films of Al-Cu alloys can be easily obtained using magnetron sputtering and are useful for such studies.29,30 However, these alloys are mostly multiphase alloys and thus their corrosion behavior remains intricate.

In the present study, a simple system was considered consisting of a pure aluminum/pure copper (Al/Cu) couple. Sample immersion for 24 h in a 10−3 M Na2SO4 solution was followed by observations with an optical and a scanning electron microscope to reveal the corrosion morphology. Particular attention was paid to the Al/Cu interface. Measurements of local potentials were carried out and compared with results obtained from calculations based on the solution of the Laplace equation to describe the first moments of immersion. On the basis of the experimental approach and the mathematical model, the interpretation of the corrosion phenomena occurring at the Al/Cu interface is proposed.

Experimental

Samples.—The sample consisted of a pure aluminum/pure copper couple. A cylinder of pure aluminum (99.999 wt %), provided by Alfa/Aesar, was drilled in its center and a cylinder of pure copper (99.9 wt %), provided by Goodfellow, was then introduced by force into the hole. The assembly of the two materials gave a perfectly joined interface, avoiding any crevice corrosion due to surface defects. The diameters of the two cylinders were chosen to obtain a ratio aluminum surface area/copper surface area of 10 (external diameters were equal to 10 and 3.15 mm for aluminum and copper bars, respectively). The electrode was then embedded in an epoxy resin so that a disk electrode was obtained at the extremity.

Before immersion in the electrolyte, the disk electrode was mechanically polished with SiC papers up to 4000 grade and ultrasonically cleaned with ethanol, then with distilled water. The electrolyte was a 10−3 M Na2SO4 solution prepared with analytical grade chemicals in contact with an air atmosphere and at room temperature.

Local electrochemical measurements.—Local electrochemical measurements were performed using a homemade device. The local...
potential variations were measured using a 100 μm diameter Ag/AgCl microelectrode. It consisted of a Ag wire (100 μm in diameter, Goodfellow) laterally insulated with cataphoretic paint and sealed in a glass capillary with epoxy resin. The AgCl was deposited in a 2 M KCl solution under potentiostatic oxidation of the Ag electrode at 0.4 V/SCE. The microreference electrode was moved with a three-axis positioning system (UTM25, Newport) driven by a motion encoder (MM4005, Newport) allowing a spatial resolution of 0.2 μm in the three directions. A homemade analog differential amplifier with both variable gain and high input impedance was used to record the local potential. All measurements were performed at the corrosion potential \( E_{corr} \) using a Keithley 2000 digital multimeter. The experimental setup was controlled with homemade data-acquisition software developed under a LabView environment.

**Surface characterizations.**— The samples were observed before and after 24 h of immersion in a 10\(^{-3}\) M Na\(_2\)SO\(_4\) solution by optical microscopy with an Olympus PMG3 microscope. Observations with a scanning electron microscope were also performed using a Leo 435VP apparatus to obtain a better description of the corrosion morphology, particularly at the Al/Cu interface.

**Theoretical Description of the Current and Potential Distributions**

**Mathematical model.**— Numerical simulations were performed to obtain a description of the potential and current distributions on the surface of the disk electrode and in the surrounding electrolyte solution at the beginning of immersion. Figure 1 gives a schematic representation of the disk electrode used in this study.

The potential \( \Phi \) in the solution surrounding the electrode is governed by the Laplace equation

\[
\nabla^2 \Phi = 0 \tag{1}
\]

Using cylindrical coordinates \((r, \theta, z)\), Eq. 1 can be expressed as

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \Phi}{\partial r} \right) + \frac{1}{r^2} \frac{\partial^2 \Phi}{\partial \theta^2} + \frac{\partial^2 \Phi}{\partial z^2} = 0 \tag{2}
\]

where \( z \) is the normal distance to the electrode surface, \( r \) is the radial coordinate, and \( \theta \) is the azimuth. The cylindrical symmetry condition requires the geometry to be invariant under rotation about the \( y \) axis, i.e.,

\[
\frac{\partial \Phi}{\partial \theta} = 0 \tag{3}
\]

The combination of Eq. 2 and 3 yields the governing equation in a two-dimensional (2D) domain as

\[
\frac{\partial^2 \Phi}{\partial r^2} + \frac{1}{r} \frac{\partial \Phi}{\partial r} + \frac{\partial^2 \Phi}{\partial z^2} = 0 \tag{4}
\]

On the surrounding insulator and far from the electrode surface, the boundary conditions are given by

\[
\frac{\partial \Phi}{\partial r} \bigg|_{r=r_0} = 0 \quad \text{at} \quad r > r_0 \tag{5}
\]

and

\[
\Phi \to 0 \enspace \text{as} \enspace r^2 + z^2 \to \infty \tag{6}
\]

Under the assumption of a kinetic regime, the current density at the electrode surface can be expressed as

\[
I = -k \frac{\partial \Phi}{\partial z} \bigg|_{z=0} \tag{7}
\]

where \( k \) is the electrolyte conductivity.

The boundary conditions were determined from experimental measurements performed individually on each material. On the aluminum part of the electrode, the boundary condition corresponds to an anodic current of 1 μA cm\(^{-2}\). On the copper electrode, both oxygen reaction and copper dissolution were taken into account. The global current can be expressed as

\[
I_{Cu} = k_{Cu} \exp \left( \frac{2.303}{b_{Cu}} \times \Phi \right) - k_{O_2} \exp \left( \frac{2.303}{b_{O_2}} \times \Phi \right) \tag{8}
\]

where the constants \( k_{Cu} \) and \( k_{O_2} \) are determined from experimental measurements of both the corrosion potential of the Cu electrode and the anodic and cathodic Tafel slopes of copper dissolution and oxygen reduction (\( b_{Cu} \), \( b_{O_2} \)) respectively. The values determined experimentally were: \( E_{corr} = -0.610 \) V/SCE, \( b_{Cu} = 55 \) mV/dec, and \( b_{O_2} = 220 \) mV/dec, allowing calculation of the constants \( k_{Cu} = 9.4 \) A cm\(^{-2}\), and \( k_{O_2} = 7.6 \times 10^{-6} \) A cm\(^{-2}\).

The simulations were performed using a finite element package Femlab in a 2D axial symmetry. The mesh size was refined to obtain a numerical error lower than 0.1% evaluated from the net current of the system, which is the sum of the current passing through the copper and aluminum electrodes.

**Results of the simulations.**— Figure 2 shows the potential distribution calculated on the electrode surface along the electrode radius with the electrolyte conductivity as a parameter. Independently of the electrolyte conductivity, the general shape of the potential distribution remains similar. The potential is seen to be constant over...
Figure 3. (Color online) Potential distributions on the surface of the Al/Cu model couple deduced from theoretical calculations for two values of the probe position (electrolyte conductivity equal to $5 \times 10^{-2}$ S m$^{-1}$).

The resolution of the Laplace equation also allows the distribution of the current on the disk electrode surface to be determined: both normal and radial current distributions were calculated as shown in Fig. 4. The normal current (Fig. 4a) on aluminum is constant and corresponds to the boundary condition chosen, while for the copper electrode, the calculations show a cathodic current distribution along the electrode radius. Thus, calculation led to results in good agreement with the initial hypothesis, a passive behavior for aluminum and a cathodic current related to oxygen reduction on copper. Furthermore, potential and current distributions revealed a particular behavior at the Al/Cu interface. Figure 4a shows a high cathodic current on copper at the Al/Cu interface corresponding to an increase of oxygen reduction on copper:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

This suggests that local variations of the chemical composition of the electrolyte can occur from the beginning of immersion with a local alkalinization of the electrolyte at the Al/Cu interface. Figure 4b also shows an increase of the radial component of the current over the aluminum in the vicinity of the interface between the two metals. The variations of the radial contribution are linked to the potential distribution over the aluminum, whereas for a constant value of the potential at the electrode surface (for instance over the copper electrode as shown in Fig. 3) the normal contribution of the current varies from the electrode center to the Cu interface (Fig. 4a) and the radial current contribution is zero. These results suggested a particular evolution of the interface morphology of the disk electrode after immersion in the electrolyte related to corrosion phenomena restricted to the Al/Cu interface.

**Results and Discussion**

**Morphology of the Al/Cu interface after 24 h of immersion in a $10^{-3}$ M $Na_2SO_4$ solution.**— The Al/Cu interface was observed using optical microscopy and SEM before and after immersion in the sodium sulfate solution. Figure 5 shows an optical micrograph of the interface before immersion (copper on the right and aluminum on the left of the micrograph). The two materials are perfectly joined without any defects observable at the interface. After 24 h of immersion in the sulfate solution (Fig. 6a), two main differences were observed in the vicinity of the interface by comparison with the observations performed before immersion.

1. A deep crevice was formed at the Al/Cu interface. Close to the crevice, aluminum presents a bright color, while, except in this zone, it seems to be covered by an oxide film over its whole surface, which is in good agreement with previous hypotheses concerning a passive state for aluminum in the couple. The bright color suggests that the crevice was at least partially related to the dissolution of the aluminum close to the interface.

2. An orange-brown ring of about 50 μm thick occurred all around the Al/Cu interface. It was located on the aluminum material at a distance of about 150 μm from the interface. The ring was
analyzed by EDS as being copper and is attributed to the redeposition of copper coming from the dissolution of the Al/Cu interface.31,32

The observations also show that the corrosion processes were restricted to the Al/Cu interface and only concerned the interface or the zone close to the interface (copper ring at 150 μm from the interface). No other domain of the sample exhibited corrosion damage, whether on aluminum or copper. Moreover, Fig. 6b clearly shows that the corrosion phenomenon is independent of the size of the interface involved in the reaction process. Similar phenomena were observed around a 10 μm particle of copper which became embedded in the aluminum part of the electrode during mechanical polishing. The particle and its surrounding aluminum also behave as a microcouple. The formation of a crevice is seen at the Al/Cu interface and copper redeposition occurred on the aluminum part not far from the copper particle. Furthermore, these results are in good agreement with those obtained on AA2024, in which Al2CuMg particles act as copper sources after immersion in sulfate solutions with or without chlorides.13

Further SEM observations allow the zone close to the interface to be more accurately described. In Fig. 7a and b, the gray zone corresponds to aluminum while the white zone corresponds to copper. The deep crevice previously observed using optical microscopy was more accurately seen on the SEM micrographs. Moreover, aluminum was found to be corroded close to the Al/Cu interface, with a dissolution depth decreasing from the interface to some micrometers from the interface (Fig. 7a). Except in this zone, aluminum was not corroded. Similar observations were performed for copper, for which no corrosion damage on the copper disk except at the Al/Cu interface was seen (Fig. 7b). Accurate analysis of the topography of the copper at the interface gave striking results for the corrosion process. At the Al/Cu interface, copper formed a kind of ledge, with no corrosion damage on the copper disk surface but a strong dissolution of copper at the Al/Cu interface, suggesting the occurrence of crevice corrosion of copper.33

Comparison between theoretical calculations and experimental observations.—Observations of the morphology of the Al/Cu interface after immersion in the electrolyte suggest that corrosion occurs in different steps. The strong dissolution of aluminum at the Al/Cu

Figure 5. (Color online) Optical observation of the Al/Cu interface of the disk electrode before immersion.

Figure 6. (Color online) Optical observations after 24 h of immersion in a 10−3 M Na2SO4 solution of (a) the Al/Cu interface and (b) a copper particle embedded in pure aluminum on the disk electrode.

Figure 7. SEM observations of the Al/Cu interface of the disk electrode after 24 h of immersion in a 10−3 M Na2SO4 solution: (a) and (b) show two different views of the crevice.
Thus, due to the strong cathodic reduction, alkalinization of the dissolution can be ignored during the first moments of immersion on the copper electrode close to the Al/Cu interface, whereas copper distribution shows that a significant oxygen reduction occurs phenomena observed on the aluminum/copper model couple. A three-step mechanism is proposed to explain the corrosion phenomena associated with copper-rich intermetallics in aluminum alloyes. The results show that studying such a simple system as the pure aluminum/pure copper couple is relevant to understand the corrosion phenomena associated with copper-rich intermetallics in aluminum alloys. The potential and current distributions on the surface of the model couple were deduced from theoretical calculations and the potential distribution was checked using a Ag/AgCl microreference electrode. Increased cathodic activity related to oxygen reduction was observed at the Al/Cu interface from the beginning of immersion. Combination of the measurements and calculations with optical and SEM observations of the model couple after a longer immersion time (24 h) allowed a three-step mechanism to be proposed.
to explain the corrosion damage. In this mechanism, the formation of a copper deposit, always observed on commercial copper-rich aluminum alloys, does not appear to be the main step of the process but only a consequence of the corrosion damage. Our work underlines that the local alkalization of the electrolyte at the Al/Cu interface plays a key role in the degradation of the system.

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