



# Surface study of films formed on copper and brass at open circuit potential

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## ABSTRACT

The corrosion resistance of Cu–Zn alloys strongly depends on the quality of the protective passive film. This study focuses on the influence of Zn on the composition of oxide films on copper and brass (Cu77Zn21Al2) in borax 0.1 mol L<sup>-1</sup> (pH 9.2) solution, where the solubility of copper oxides is minimal. The effect of the presence of chloride ions at low concentration (0.01 mol L<sup>-1</sup>) in the electrolyte was also evaluated. Both conditions were studied using a set of different electrochemical, optical and surface techniques such as cyclic voltammetry, differential reflectance, X-ray photoelectron spectroscopy and Raman spectroscopy. A duplex Cu<sub>2</sub>O/CuO layer forms on copper at potentials positive to the open circuit potential (OCP), while in the case of brass, zinc compounds are also incorporated to the surface film. It also became evident that a surface film can be formed on these materials even at potentials negative to the OCP. Zn(II) species are the main constituents of the films growing on brass, while copper oxides are incorporated to the surface film when approaching the OCP. The presence of chloride ions at low concentrations contributes to the dissolution of the oxo-hydroxides formed during the early stages of the aging process at open circuit potential. Also, copper chloro-compounds are formed, as shown by Raman spectroscopy for both copper and brass electrodes.

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## 1. Introduction

Copper and brass alloys are materials broadly used in many basic and applied research areas, such as chip design for computers, printed circuit boards, transistor systems, and in power generation industries as condenser and heat exchanger tubes. For these reasons, there is a permanent interest in studying the passivity of both materials and the surface layers formed in different conditions [1–10].

The composition and performance of the passive layer formed on copper in aqueous solutions depends on many variables such as pH, applied potential, polarization time, presence of aggressive anions and aerating conditions.

It is well known that both, cuprous and cupric oxides are present in most passive layers. Often, distinction between both oxides is quite tricky for these systems. Besides, when chloride ions are present in aqueous solutions, copper and brass are susceptible to develop pitting corrosion and brass may experience dealloying. In our previous works [11,12] we studied the composition of the passive layer on copper and brass with emphasis on the electrical properties and their influence in the oxygen reduction reaction. We also observed that in brass, when Zn is incorporated to Cu, the

properties and the thickness of the surface film change. The films grown on brass at open circuit potential tend to be thicker but less resistive and Zn compounds incorporate to those films. The effect of chloride ions on the surface film is the chemical dissolution of copper and zinc compounds, leading to the formation of more stable chloro-compounds. The purpose of this work is to deepen the investigation on the composition of the films formed on copper and brass at open circuit potential in borax 0.1 mol L<sup>-1</sup> and to better understand the effect of the presence of chloride ions in the electrolyte. For this purpose, *in situ* and *ex situ* surface analytical methods such as differential reflectance (DR), X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy have been used [13–17] and complemented with electrochemical experiments.

## 2. Experimental setup

### 2.1. Materials and solutions

Copper (spectroscopic grade: 99.99%) and aluminum-brass rods (77% Cu, 21% Zn, 2% Al; UNS 68700) provided by Metals Sample, USA and LCL Pty Ltd<sup>TM</sup>, Australia respectively, were used as working electrodes. Metal disks were embedded in epoxy resin and mounted on PVC holders, with a cable as electrical contact welded at the back side of the disk and isolated from electrolyte. Prior to use, the exposed electrodes surface were abraded with a sequence of emery papers and then mirror polished with 0.5 μm

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alumina powder and polishing cloth, and finally rinsed with deionized water (Millipore™). When performing hydrodynamical tests, rotating-disk electrodes were prepared from rods of Cu and brass, which were embedded in epoxy resin and mounted in Grilon™ cylindrical holders.

The following solutions were used as working electrolytes for the experiments: borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ )  $0.1 \text{ mol L}^{-1}$  (pH 9.2) and borax  $0.1 \text{ mol L}^{-1}$  + NaCl  $0.01 \text{ mol L}^{-1}$ , the latter to investigate chloride ions effect on film properties. At this pH value, the solubility of the corrosion products formed on the electrode surface is low. The solutions were deaerated for 15 min with high-purity  $\text{N}_2$  or saturated with  $\text{O}_2$  during 15 min prior to each measurement, as indicated where necessary. All the experiments were carried out at room temperature ( $20 \pm 2^\circ\text{C}$ ). Sigma–Aldrich® ultra pure reagents and deionized water by Millipore™ were used to prepare the solutions.

## 2.2. Electrochemical measurements

A conventional three-electrode chemical cell was employed for electrochemical measurements. Potentials were measured against  $\text{Hg}/\text{Hg}_2\text{SO}_4/\text{K}_2\text{SO}_4$   $0.6 \text{ mol L}^{-1}$  (MSE,  $0.616 \text{ V}$  vs NHE; Schott Instruments™, Germany) for the electrochemical experiments and  $\text{Ag}/\text{AgCl}/\text{NaCl}$   $3 \text{ mol L}^{-1}$  ( $0.208 \text{ V}$  vs NHE; Radiometer Analytical™, France) when recording reflectance spectra. However, all the potential values are indicated taking MSE as reference. A Voltalab PGP 201 (Radiometer Analytical™) potentiostat was employed to control current and potential.

Cyclic voltammograms were recorded after deaerating the solutions for 15 min with high-purity  $\text{N}_2$ . The electrodes were then pretreated by holding them at  $-1.6 \text{ V}$  for 10 min to have a reproducible initial condition. Hydrodynamical voltammograms were carried out using a rotating disc electrode EDI101 with a speed control unit CTV101, both by Radiometer Analytical™.

## 2.3. Spectroscopic measurements

The surface analysis of each surface was carried out after 24 h at OCP in  $\text{O}_2$  saturated  $0.1 \text{ mol L}^{-1}$  borax solutions (with and without chloride ions added).

First, the composition of the surface films formed at the open circuit potential (OCP) on the electrodes aged in both electrolytes was evaluated using reflectance spectroscopy. The spectroelectrochemical measurements were carried out using a commercial double-beam spectrophotometer (Shimadzu UV 160A), modified as described elsewhere [17]. The transmittance spectra were recorded *in situ*. Baseline corrections were carried out by polarizing two identical polished surfaces at  $-1.6 \text{ V}$  to prevent oxide growth in  $\text{N}_2$  saturated electrolyte.

Then, XPS analysis of the aged electrodes was performed on samples aged in both electrolytes using a VG Microtech ESCA3000 (monochromatic  $\text{Al K}\alpha$  radiation of  $1486.7 \text{ eV}$  with a primary beam energy of  $15 \text{ kV}$  and an electron current of  $5 \text{ A}$ ) at Laboratório de Superfícies e Interfaces (Universidade Federal do Paraná, Curitiba, Brazil). The base pressure inside the chamber was  $3 \times 10^{-10} \text{ mbar}$ , and the spectra were performed close to  $45^\circ$  of take-off angle respect to the surface normal to the sample, using  $0.8 \text{ eV}$  of energy resolution for the hemispherical energy analyzer. The samples were inserted into the chamber after 1 day of pressure stabilizing. Samples spectra were collected for the following core levels:  $\text{Cu}2\text{p}$ ,  $\text{Zn}2\text{p}$ ,  $\text{O}1\text{s}$ ,  $\text{C}1\text{s}$  and  $\text{Cl}2\text{p}$  as well as  $\text{Cu}_{\text{LMM}}$  and  $\text{Zn}_{\text{LMM}}$  Auger lines, separately with an energy resolution of  $\pm 0.1 \text{ eV}$ . The binding energy scale was calibrated using  $\text{C}1\text{s}$  binding energy to  $284.5 \text{ eV}$  in order to compensate the electrostatic charging [18].

Moreover, the aged electrodes were also examined by Raman spectroscopy, using an Invia Reflex confocal Raman microprobe.

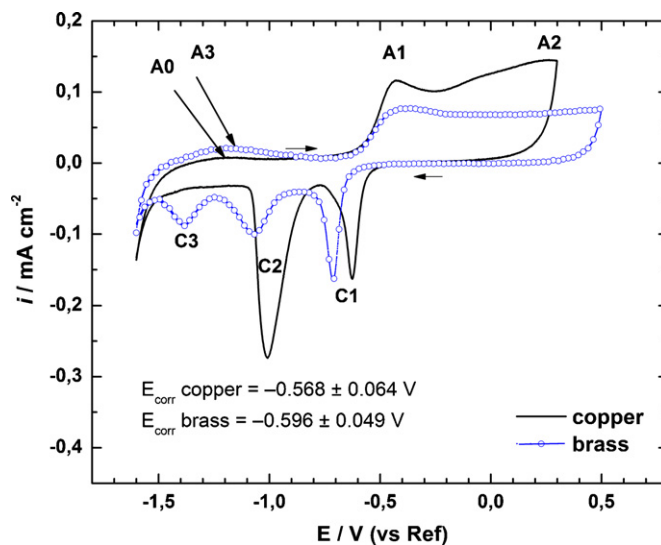


Fig. 1. CVs recorded for copper and brass in deaerated borax  $0.1 \text{ mol L}^{-1}$ .  $\nu = 0.02 \text{ V s}^{-1}$ .

Excitation was provided with the  $514 \text{ nm}$  emission line of an  $\text{Ar}^+$  laser. Measurements were performed in the backscattering mode using a  $50\times$  objective at 50 and 100% power source.

## 3. Results and discussion

### 3.1. Surface characterization by electrochemical techniques

The current–potential curves, recorded by cyclic voltammetry (CV) for copper and brass in deaerated borax solutions are shown in Fig. 1. In the case of copper, the CV shows three peaks during the positive scan. The one at  $-1.20 \text{ V}$  (A0) can be attributed to the formation of adsorbed species such as  $\text{Cu}(\text{H}_2\text{O})_{\text{ads}}$  and/or  $\text{Cu}(\text{OH})_{\text{ads}}^-$  on the electrode surface [19–21]:



The other one, at  $-0.45 \text{ V}$ , can be ascribed to  $\text{Cu}_2\text{O}$  formation (A1). Then,  $\text{Cu}_2\text{O}$  oxidation to  $\text{CuO}$  (A2) is responsible for the current increase starting at about  $-0.25 \text{ V}$ . The two negative peaks are located at  $-0.62 \text{ V}$  ( $\text{CuO}$  reduction to  $\text{Cu}_2\text{O}$ ; C1) and  $-1.00 \text{ V}$  ( $\text{Cu}_2\text{O}$  reduction; C2). The cyclic voltammogram of brass shows a broad positive band at  $-1.20 \text{ V}$  (A3), another one at  $-0.40 \text{ V}$  (A1) and a plateau starting at  $-0.15 \text{ V}$  (A2). These can be attributed to the following processes, as deduced by comparison with the voltammogram of copper (Fig. 1) and pure Zn [22–24] (not shown):

A3:  $\text{Cu}(\text{H}_2\text{O})/\text{Cu}(\text{OH})_{\text{ads}}^-$  monolayer on the surface, plus a  $\text{ZnO}$  film.

A1:  $\text{Cu}$  oxidation to  $\text{Cu}_2\text{O}$ .

A2:  $\text{Cu}_2\text{O}$  oxidation to  $\text{CuO}$ .

The compounds responsible for the appearance of peaks A1 and A2 constitute a duplex passive film which explains the broad plateau observed up to  $0.50 \text{ V}$  [25,32].

As regards negative peaks, three peaks can be seen associated to the following processes:

C1:  $\text{CuO}$  reduction to  $\text{Cu}_2\text{O}$ , at  $-0.70 \text{ V}$ .

C2:  $\text{Cu}_2\text{O}$  reduction to  $\text{Cu}$  at  $-1.10 \text{ V}$ .

C3:  $\text{HCuO}_2^-$  reduction at  $-1.35 \text{ V}$  [25,26],  $\text{ZnO}$  and soluble  $\text{Zn}(\text{II})$  species reduction formed during the positive scan (in

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