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# 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  $\mu$ m

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alumina powder and polishing cloth, and finally rinsed with deionized water (Millipore<sup>TM</sup>). 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<sup>TM</sup> cylindrical holders.

The following solutions were used as working electrolytes for the experiments: borax (Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>·10H<sub>2</sub>O) 0.1 mol L<sup>-1</sup> (pH 9.2) and borax 0.1 mol L<sup>-1</sup> + NaCl 0.01 mol L<sup>-1</sup>, 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 N<sub>2</sub> or saturated with O<sub>2</sub> during 15 min prior to each measurement, as indicated where necessary. All the experiments were carried out at room temperature ( $20 \pm 2^{\circ}$ C). Sigma–Aldrich<sup>®</sup> ultra pure regents and deionized water by Millipore<sup>TM</sup> 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  $Hg/Hg_2SO_4/K_2SO_4$  0.6 mol  $L^{-1}$  (MSE, 0.616 V vs NHE; Schott Instruments<sup>TM</sup>, Germany) for the electrochemical experiments and Ag/AgCl/NaCl 3 mol  $L^{-1}$  (0.208 V vs NHE; Radiometer Analytical<sup>TM</sup>, France) when recording reflectance spectra. However, all the potential values are indicated taking MSE as reference. A Voltalab PGP 201 (Radiometer Analytical<sup>TM</sup>) potentiostat was employed to control current and potential.

Cyclic voltammograms were recorded after deaerating the solutions for 15 min with high-purity  $N_2$ . The electrodes were then pretreated by holding them at -1.6 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<sup>TM</sup>.

#### 2.3. Spectroscopic measurements

The surface analysis of each surface was carried out after 24 h at OCP in  $O_2$  saturated 0.1 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 V to prevent oxide growth in N<sub>2</sub> saturated electrolyte.

Then, XPS analysis of the aged electrodes was performed on samples aged in both electrolytes using a VG Microtech ESCA3000 (monochromatic Al K $\alpha$  radiation of 1486.7 eV with a primary beam energy of 15 kV and an electron current of 5 A) at Laboratório de Superfícies e Interfases (Universidade Federal do Paraná, Curitiba, Brazil). The base pressure inside the chamber was  $3 \times 10^{-10}$  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 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: Cu2p, Zn2p, O1s, C1s and Cl2p as well as Cu<sub>LMM</sub> and Zn<sub>LMM</sub> Auger lines, separately with an energy resolution of  $\pm 0.1$  eV. The binding energy scale was calibrated using C1s binding energy to 284.5 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  $0.1 \text{ mol } L^{-1}$ .  $v = 0.02 \text{ V s}^{-1}$ .

Excitation was provided with the 514 nm emission line of an Ar<sup>+</sup> 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 V (A0) can be attributed to the formation of adsorbed species such as Cu(H<sub>2</sub>O)<sub>ads</sub> and/or Cu(OH)<sup>-</sup><sub>ads</sub> on the electrode surface [19–21]:

$$Cu + H_2O \leftrightarrows Cu(H_2O)_{ads} \tag{1}$$

$$Cu + OH^{-} \leftrightarrows Cu(OH)^{-}_{ads}$$
<sup>(2)</sup>

The other one, at -0.45 V, can be ascribed to Cu<sub>2</sub>O formation (A1). Then, Cu<sub>2</sub>O oxidation to CuO (A2) is responsible for the current increase starting at about -0.25 V. The two negative peaks are located at -0.62 V (CuO reduction to Cu<sub>2</sub>O; C1) and -1.00 V (Cu<sub>2</sub>O reduction; C2). The cyclic voltammogram of brass shows a broad positive band at -1.20 V (A3), another one at -0.40 V (A1) and a plateau starting at -0.15 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:  $Cu(H_2O)/Cu(OH)^-$  monolayer on the surface, plus a ZnO film. A1: Cu oxidation to Cu<sub>2</sub>O. A2: Cu<sub>2</sub>O oxidation to 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 V [25,32].

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

- C1: CuO reduction to  $Cu_2O$ , at -0.70V.
- C2:  $Cu_2O$  reduction to Cu at -1.10 V.
- C3:  $HCuO_2^-$  reduction at -1.35V [25,26], ZnO and soluble Zn(II) species reduction formed during the positive scan (in



Fig. 2. CVs recorded for copper and brass in deaerated borax  $0.1 \text{ mol } L^{-1}$  + NaCl 0.01 mol  $L^{-1}$ . v = 0.02 V s<sup>-1</sup>.

agreement with observations published earlier by Ismail et al. [19] for Cu-24Zn in borate-boric acid pH 9.0).

The presence of  $HCuO_2^-$  has been observed when the most positive limit of the potential scan is higher than 0.20V vs MSE [20,21]. In this case, the intensity of peak C3 increases with increasing anodization time up to E > 0.50 V, where formation of soluble species is expected.  $HCuO_2^-$  has been shown to form by hydration and can be reduced directly to Cu, as presented in reactions (3) and (4):

$$CuO + H_2O \leftrightarrows HCuO_2^{-} \tag{3}$$

$$HCuO_2^- + 3H^+ + 2e^- \leftrightarrows Cu + 2H_2O \tag{4}$$

When chloride ions are added to the electrolyte, new peaks are observed for both materials (Fig. 2). For copper, a new positive peak appeared at -0.55 V (A4) due to copper-chloride compounds, associated to a new negative shoulder labeled as C4. As regards the negative peaks, the one at -0.62 V is due to CuO reduction (C1), the next one at -0.68 V can be attributed to copper-chloride species (C4; probably *atacamite*: Cu<sub>2</sub>(OH)<sub>3</sub>Cl [2]), whereas the one at about -1.00 V is ascribed to Cu<sub>2</sub>O reduction to Cu (C2).

In saline solutions (as in seawater) several complex compounds may form, such as nantokite (CuCl), eriochalcite (CuCl<sub>2</sub>), atacamite and/or clinoatacamite (Cu<sub>2</sub>(OH)<sub>3</sub>Cl). The presence of the latter is probable in the present system. The unusual effects that occur in the presence of chloride anions in the electrolyte are related to the changes it produces in the oxide layers. It is well-known that Cu<sub>2</sub>O is soluble in chloride solutions due to the formation of CuCl<sub>2</sub><sup>-</sup> and CuCl<sub>3</sub><sup>2-</sup>. So, the two main processes described below are in competition.

When no chloride ions are present [22],

$$Cu_2O + H_2O \leftrightarrows 2Cu(I) + 2OH^-$$
(5)

(I)

$$\log[Cu(I)] = -0.84 - pH$$

Given that pH = 9.2, then  $[Cu(I)] = 9.12 \times 10^{-11} \text{ mol } L^{-1}$ . Instead, when chloride ions are present [24],

$$Cu_2O + 4Cl^- + H_2O \leftrightarrows 2CuCl_2^- + 2OH^-$$
(6)

$$K = \frac{([CuCl_2^{-}]^2[OH^{-}]^2)}{[Cl^{-}]^4} = 3.98 \times 10^{-18}$$
(II)



**Fig. 3.** CVs for copper in stagnant (a) and 600 rpm rotation speed (b) in deaerated borax 0.1 mol  $L^{-1}$ . v = 0.02 V s<sup>-1</sup>.

Taking  $[CI^-] = 0.01 \text{ mol } L^{-1}$  and  $[OH^-] = 1.58 \times 10^{-5} \text{ mol } / L$  (pH = 9.2) and replacing in (II), it follows that  $[CuCl_2^-] = 1.26 \times 10^{-8} \text{ mol } L^{-1}$ . This means that the solubility of Cu<sub>2</sub>O in chloride-rich electrolytes is higher than that in water, and so the formation of aqueous chloro-compounds is the predominant process.

For brass, when chloride ions are present, peak A1 in the voltammogram is not well-defined, while the cathodic peaks shift to more negative potentials. In this case, the shoulder C4 is located at about -0.83 V. At the same time, the currents are slightly higher in the presence of chloride ions, which can be attributed to a higher surface roughness due to partial dissolution resulting from the complexing effect of chloride ions. Also, it has been argued that chloride ions enhance the dissolution of copper oxides by reduction in the presence of Zn, by means of reactions (7) and (8) [27,28]

$$Cu_2O + Zn + 2Cl^- + H_2O = 2Cu + Zn(OH)_2Cl_2^{2-}$$
 (7)

 $CuO + Zn + 2Cl^{-} + H_2O \equiv Cu + Zn(OH)_2Cl_2^{2-}$  (8)

The formation of soluble species on the electrodes can be evaluated using a rotating disc electrode to record cyclic voltammograms at different rotation rates. The absence of a cathodic peak implies that the species oxidized during the positive scan were dissolved into solution, before being reduced on the reverse scan. Fig. 3 shows two voltammograms recorded in deaerated borax solution, comparing a stationary and a rotating copper electrode. An important feature observed is the decrease in the current intensities associated to the voltammetric peaks, due to the rotation effect. As soluble species move away from the electrode, they cannot be reduced. However, the negative peaks are still present, suggesting that not only soluble species are formed. The results obtained for brass are shown in Fig. 4. In this case, for the stagnant electrolyte three anodic and three cathodic processes are observed, as discussed above. With rotation, as was the case for copper, a drop in the charge is observed for the reduction peaks. Furthermore, peak C3 can no longer be observed. Given that this peak was assigned to the electroreduction of soluble species such as  $HCuO_2^{-}$  and Zn(II)compounds, the absence is in agreement with the expected behavior. The remaining current density observed at negative potentials is due to ZnO reduction. An interesting result is the separation of C1 under hydrodynamic control. Two peaks are clearly observed that can be attributed to the reduction of CuO and  $Cu(OH)_2$  at -0.73 and -0.68 V. Cupric hydroxide is relatively soluble in alkaline



Fig. 4. CVs for brass in stagnant (a) and 600 rpm rotation speed (b) in deaerated borax 0.1 mol  $L^{-1}$ .  $\nu$  = 0.02 V s<sup>-1</sup>.

solutions due to the formation of soluble species such as the cuprate ions,  $[Cu(OH)_4]_2^-$  or  $CuO_2^{2-}$ . The fraction of  $Cu(OH)_2$  dissolved as cuprate ions moves away from the electrode and so is less likely to be reduced on the electrode during a hydrodynamic cathodic polarization sweep, resulting in the lower intensity of reduction peak C1.

# 3.2. Surface characterization based on spectroscopic techniques

#### 3.2.1. Differential reflectance

This *in situ* technique enables the acquisition of transmittance spectra at characteristic potentials, which were selected from cyclic voltammograms. Here it was used to obtain spectroscopic information of species at selected increasing potentials and at OCP.

Fig. 5 presents the spectra for copper held 24 h at OCP in deaerated borax  $0.1 \text{ mol } L^{-1}$  with and without chloride ions, and polarized at E = -0.4 and E = 0.2 V for 5 h in deaerated borax  $0.1 \text{ mol } L^{-1}$ . These two potential values were chosen because they are characteristic potentials where  $Cu_2O$  and CuO can be grown, respectively. At 320 nm there is a "discontinuity" in every signal (even the baseline) as the spectrophotometer changes lamps (from



Fig. 5. Differential reflectance obtained for  $Cu_2O$ , CuO and OCP of copper electrode immersion in deaerated borax 0.1 mol  $L^{-1}$  without and with NaCl 0.01 mol  $L^{-1}$  added.



**Fig. 6.** Differential reflectance obtained for  $Cu_2O$ , CuO and OCP of brass electrode immersion in deaerated borax 0.1 mol  $L^{-1}$  without and with NaCl 0.01 mol  $L^{-1}$  added.

Vis to UV). The spectrum for Cu<sub>2</sub>O shows a shoulder at ~560 nm (due to upper *d*-band transition toward conduction bands above the Fermi level:  $E_m$ , upper  $\rightarrow E_F$  as indicated in literature [29–31]). A broad band from 215 to 250 nm (observed also by Shanley et al. [31] at 242 nm) is another characteristic feature due to presence of Cu<sub>2</sub>O. The spectrum recorded after the electrode has been kept 5 h at 0.20 V is dominated by a peak at 280 nm which is distinctive for CuO (observed at 300 nm in Fig. 5). However the presence of a duplex Cu<sub>2</sub>O/CuO film is confirmed by the coexistence of the most characteristic peaks and bands from Cu<sub>2</sub>O. Similar results were presented by J.B. He et al. [32] who studied the potential dependence of cuprous/cupric duplex film growth on a copper electrode in alkaline media on the time scale from 1 to 30 min, by XRD, XPS, voltammetry, chronopotentiometry and capacity measurements.

On the other hand, the transmittance spectrum of copper held at OCP only shows the main characteristic peaks and bands due to  $Cu_2O$  [17]. This is in agreement with the OCP value typical of copper in these conditions, where  $Cu_2O$  growth is the leading process (see  $E_{corr}$  value in Fig. 1). When chloride ions are added and the electrode is aged at OCP, the  $Cu_2O$  band in the UV region shifts to longer wavelengths. This is probably due to the incorporation of copperchloride species. Also, the relative intensities at 250 and 350 nm seem to indicate a negligible presence of CuO in the film.

The transmittance spectra recorded on brass electrodes aged at OCP and at the characteristic peak potentials in the presence of chloride ions are presented in Fig. 6. Here again, the spectra for  $Cu_2O$  and CuO grown at E = -0.4 and 0.2 V respectively are included, and show the same peaks and bands observed as in Fig. 5, but here they became smoother. Also, there is a significant difference at OCP when chloride ions are present. In borax without Cl<sup>-</sup> ions there is a strong absorbance between 500 and 800 nm (which means low transmittance values) and the spectrum is similar to that for Zn in deaerated borax  $0.1 \text{ mol } L^{-1}$  (not shown) [33]. The passivation of brass is based on the formation of a layer consisting mainly of Cu<sub>2</sub>O, CuO and ZnO. In Fig. 6, for brass at OCP without chloride ions, the presence of ZnO is associated to the intense signal at about 360 nm and to the broad and plane band that can be seen from 300 to 800 nm. ZnO incorporation to the passive layer on brass exposed to humidified air at 90% RH has been shown also by Qiu and Leygraf [10].

Also, when Cl<sup>-</sup> ions are added to the solution, the spectra shows a remarkable change in the transmittance due to the zinc oxo-hydroxides dissolution on the surface oxides layer of



**Fig. 7.** X-ray photoelectron spectra of Cu2p line for copper and brass aged at OCP for 24 h in aerated (solid lines) and deaerated (lines + symbol) borax  $0.1 \text{ mol } L^{-1}$ .

brass, demonstrated by the increment in the transmittance values between 500 and 800 nm.

#### 3.2.2. X-ray photoelectron spectroscopy and Auger spectroscopy

X-ray photoelectron spectra were recorded to investigate the films formed at OCP on copper, zinc and brass electrodes after 24 h exposure to oxygen saturated borax solution in the presence and absence of chloride ions, in order to elucidate surface composition with special attention to the oxidation states of Cu and Zn. For the sake of comparison, spectra for electrodes immersed in nitrogen saturated borax solution with the same aging conditions were taken. Because of small chemical shifts, Cu<sub>2</sub>O and ZnO peaks are not distinguishable from Cu and Zn peaks in XPS Cu2p and Zn2p spectra, respectively.

The XPS Cu2p core-level emission spectra corresponding to copper and brass in aerated and deaerated borax are presented in Fig. 7. The  $Cu2p_{3/2}$  peak for  $Cu_2O$  is located at a binding energy of 932.5 eV which is almost the same energy as that of metallic copper [1,18,34], as mentioned earlier. Fig. 7 shows a peak at 932.6 eV

due to both cuprous oxide and/or metallic copper. The fact that Cu<sub>2</sub>O was observed by the techniques discussed earlier for copper and brass aged at OCP is in agreement with the possible presence of the Cu<sub>2</sub>O Cu<sub>2</sub>p peak. Moreover, the appearance of shoulders at lower binding energies in the O1s line (not shown) for copper and brass in the absence of chloride ions indicates the presence of Cu-O and/or Zn-O compounds in the films formed on both materials [35]. Also, two peaks located at 935 and 943.5 eV (satellite peaks) due to Cu(II) species like Cu(OH)<sub>2</sub> and/or CuO are observed mainly for copper and brass electrodes aged at OCP in oxygen saturated borax electrolyte. Previous results showed that Cu(OH)<sub>2</sub> is enriched at the oxide/solution interface, whereas CuO is located mainly at the inner layer formed on copper [20,36]. This process is enhanced in the presence of oxygen, in agreement with the presence of shakeup lines observed in Fig. 7, and by comparison of the XPS spectra for copper and brass in oxygenated or deoxygenated electrolytes.

Fig. 8 shows the Cu and Zn Auger LMM spectra for copper, brass and zinc in aerated borax. The Auger Cu<sub>IMM</sub> transition peak appears at 567.8 eV for metallic copper and at 569.9 eV for Cu<sub>2</sub>O, in accordance to literature data [18]. Clearly, a noticeable peak separation is observed for Cu and Cu<sub>2</sub>O on the copper electrode. For copper, the Auger Cu<sub>LMM</sub> transition peaks at 567.9 eV (Cu metal) and 569.9 eV (Cu<sub>2</sub>O) are observed in agreement with previous results obtained for copper and some brass alloys in borax pH 9.2 [22]. In the case of the brass electrode, the Auger Cu<sub>LMM</sub> confirms the presence of  $\text{Cu}_2\text{O}$  on the passive film. The Auger  $\text{Zn}_{\text{LMM}}$  spectra for brass and zinc are also shown in Fig. 8. As for metallic Cu and Cu<sub>2</sub>O, is not possible to distinguish Zn and ZnO from Zn2p core level: 2p<sub>3/2</sub> peak of Zn is located between 1021.1 and 1021.5 eV and that of ZnO between 1021.3 and 1022.4 eV. For this reason, the use of Auger Zn<sub>IMM</sub> spectra is important. As can be seen in Fig. 8, Auger transition for metallic Zn lies at 497 eV and ZnO at 499.6 eV, in good agreement with reference data [37,38].

The Cu2p spectra of copper and brass aged at OCP for 24 h in aerated borax 0.1 mol  $L^{-1}$  in the presence of chloride ions are shown in Fig. 9. As it can be seen, no X-ray satellite peak for Cu(II) species is present, which is probably due to the formation of copper-chloride and zinc-chloride soluble species, such as:

$$Cu_2O + 4Cl^- + H_2O \leftrightarrows 2CuCl_2^- + 2OH^-$$
(6)

$$Cu + 2Cl^{-} \subseteq CuCl_{2}^{-} + e^{-}$$
(9)



Fig. 8. X-ray induced Cu<sub>LMM</sub> and Zn<sub>LMM</sub> Auger spectra for copper, brass and zinc aged at OCP for 24 h in aerated borax 0.1 mol L<sup>-1</sup>.



**Fig. 9.** X-ray photoelectron spectra of Cu2p line for copper and brass aged at OCP for 24 h in aerated borax  $0.1 \text{ mol } L^{-1} + \text{NaCl } 0.01 \text{ mol } L^{-1}$ .

$$Zn + 4Cl^{-} \leftrightarrows ZnCl_{4}^{2-} + 2e^{-}$$
(10)

It has been demonstrated that the presence of chloride ions shifts the equilibrium potential of copper and zinc dissolution in the active region due to those reactions [26,29,39]. This is in agreement with the dissolution process evidenced by the reflectance spectra for brass at OCP in presence of chloride ions and discussed earlier. Besides, the presence of insoluble chloro-compounds can be confirmed from the appearance of Cl2p peak in the survey spectrum (not shown) and from the Cl2p line in Fig. 10 for copper and brass samples aged at OCP.

## 3.3. Raman spectroscopy

Raman spectroscopy was used to study the composition of films formed on copper and brass aged for 24 h at OCP in borax  $0.1 \text{ mol } L^{-1}$ , with and without chloride ions addition.

Fig. 11 presents results for copper in chloride-free and chloridecontaminated solutions, where several peaks can be assigned to Cu<sub>2</sub>O [40,41]. The identification of CuO by this technique is difficult



**Fig. 10.** X-ray photoelectron spectra of Cl2p line for copper and brass aged at OCP for 24 h in aerated borax  $0.1 \text{ mol } L^{-1} + \text{NaCl } 0.01 \text{ mol } L^{-1}$ .



**Fig. 11.** Raman spectrum for copper aged at OCP for 24 h in aerated borax 0.1 mol L<sup>-1</sup> without and with NaCl 0.01 mol L<sup>-1</sup> added.

because Raman scattering from CuO is much weaker than that from Cu<sub>2</sub>O and the main peak in the CuO spectrum ( $635 \, \text{cm}^{-1}$ ) lies too close to one of the most intense Cu<sub>2</sub>O peaks ( $633 \, \text{cm}^{-1}$ ). When chloride ions are present, a new peak at 796 cm<sup>-1</sup> [32] is observed. This peak could be attributed to copper chloro-compounds such as *atacamite*, in agreement with the results obtained in the voltammograms.

For brass, Fig. 12 shows the spectra obtained after aging for 24 h at OCP in borax 0.1 mol  $L^{-1}$ , without and with chloride ions present. The presence of Cu<sub>2</sub>O is observed in both electrolytes.

In the case of ZnO, there are four Raman active modes (zonecenter optical phonons predicted by the group theory) which are usually labeled as A1, E2 and E1. The phonons with A1 and E1 symmetries are polar phonons and, hence, exhibit different frequencies for the transverse-optical (TO) and longitudinal-optical (LO) phonons. Nonpolar phonon modes with symmetry E2 have two distinctive wave numbers: E2 (high) which is associated with oxygen atoms and E2 (low) which is associated with the Zn sublattice. The bands that appear at 101, 437 and 574 cm<sup>-1</sup> are characteristic for ZnO [42], along with the band at 382 cm<sup>-1</sup> for A1 mode and a broad asymmetric signal at 584 cm<sup>-1</sup> for the LO mode. These are in agreement with the values for bulk and thinfilms containing ZnO [43]. Fig. 12 shows an increase in the Raman shift below 150 cm<sup>-1</sup> which can be ascribed to ZnO as discussed



**Fig. 12.** Raman spectrum for brass aged at OCP for 24 h in aerated borax 0.1 mol  $L^{-1}$  without and with NaCl 0.01 mol  $L^{-1}$  added.

earlier [44], and the other peaks are probably overlapped due to the predominant presence of copper compounds. It is worth observing that in the presence of chloride ions this band is narrower than in chloride-free solutions, indicating the dissolution effect on copper compounds, which leaves an underneath layer rich in zinc compounds.

# 4. Conclusions

The influence of the presence of Zn as alloying element and Cl<sup>-</sup> ions in the electrolyte, on the composition and properties of oxide films aged on copper and brass (Cu77Zn21Al2) in borax 0.1 mol L<sup>-1</sup> (pH 9.2) solution has been evaluated by means of electrochemical and spectroscopic techniques. The following conclusions are derived from a critical analysis of the results:

- The surface characterization by means of cyclic voltammetry showed the presence of Cu<sub>2</sub>O and CuO on copper from the early stages of aging. For brass the same corrosion products together with HCuO<sub>2</sub><sup>--</sup>, ZnO, zinc oxo-hydroxides, and Zn(II) soluble species were observed. In the presence of chloride ions, both materials showed evidence of copper-chloride species such as CuCl, CuCl<sub>2</sub> and *atacamite* Cu<sub>2</sub>(OH)<sub>3</sub>Cl.
- The surface products containing zinc are much more soluble than those with copper, as deduced from hydrodynamic cyclic voltammograms. Besides, the presence of chloride ions enhances the dissolution of surface oxo-hydroxides.
- The films formed on copper after 24 h at OCP are consistent with a Cu(1)/Cu(II) duplex layer, where Cu<sub>2</sub>O is the main constituent. The OCP value in deaerated solutions is close to the potential where Cu<sub>2</sub>O starts to grow. On brass, zinc oxo-hydroxides incorporate to a great extent to the films grown at OCP, as observed from reflectance spectra.
- For copper and brass in borax chloride-free solutions the presence of Cu<sub>2</sub>O and oxo-hydroxides was confirmed by *ex situ* techniques such as XPS. When chloride ions were present, XPS spectroscopy showed the presence of insoluble copper-chloride compounds on the films formed at OCP on both materials. On the other hand, Raman spectroscopy showed a band typical of copper chlorocompounds such as *atacamite*, and the presence of ZnO on brass in absence of chloride ions.

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