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Influence of BSA adsorption on the oxide layers developed on 70Cu-30Ni alloy in static artificial seawater* 

B. Torres¹, A. Seyeux¹, S. Zanna¹, B. Tribollet², P. Marcus¹ and I. Frateur¹,²

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Abstract – Copper alloys usually used in cooling circuits of industrial plants can be affected by biocorrosion induced by biofilm formation. The global objective is to study the influence of biomolecules adsorption, which is the first step in biofilm formation, on the electrochemical behaviour of 70Cu-30Ni (wt. %) alloy and the chemical composition of oxide layers. In this work, the chosen biomolecule was the bovine serum albumin (BSA, model protein) and electrochemical measurements performed after 1 h of immersion in static artificial seawater were combined to surface analyses. In the presence of BSA, the charge transfer resistance deduced from EIS data at $E_{\text{corr}}$ is higher, corresponding to lower corrosion current. Without BSA, two oxidized layers are shown by XPS and ToF-SIMS: an outer layer mainly composed of copper oxide (Cu$_2$O redeposited layer) and an inner layer mainly composed of oxidized nickel, with a global thickness of $\sim$30 nm. The presence of BSA leads to a mixed oxide layer (CuO, Cu$_2$O, Ni(OH)$_2$) with a lower thickness ($\sim$10 nm). Thus, the protein induces a decrease of the dissolution rate at $E_{\text{corr}}$ and hence a decrease of the amount of redeposited Cu$_2$O and of the oxide layer thickness.

Key words: Copper alloy / seawater / protein adsorption / EIS / XPS / ToF-SIMS

Résumé – Effet de l'adsorption de BSA sur les couches d'oxydes développées sur l’alliage Cu70-Ni30 en eau de mer artificielle statique. Les alliages de cuivre habituellement utilisés dans les circuits de refroidissement de centrales électriques peuvent être affectés par la biocorrosion induite par la formation d’un biofilm. L’objectif global de ce travail est d’étudier l’influence de l’adsorption de biomolécules, qui est l’étape initiale de formation du biofilm, sur le comportement électrochimique de l’alliage 70Cu-30Ni (% massiques) et sur la composition chimique des couches d’oxydes. Dans ce travail, la biomolécule choisie est l’albumine de sérum bovin (BSA, protéine modélée) et des mesures électrochimiques réalisées après 1 h d’immersion en eau de mer artificielle statique ont été combinées à des analyses de surface. En présence de BSA, la résistance de transfert de charge estimée par impédance électrochimique (EIS) à $E_{\text{corr}}$ est plus élevée, correspondant à un courant de corrosion plus faible. Sans BSA, deux couches d’oxydes sont mises en évidence par XPS et ToF-SIMS : une couche externe principalement composée d’oxyde de cuivre (couche de redéposition de Cu$_2$O) et une couche interne principalement composée de nickel oxydé (épaisseur globale : $\sim$30 nm). La présence de BSA conduit à une couche mixte d’oxydes (CuO, Cu$_2$O, Ni(OH)$_2$), d’épaisseur plus faible ($\sim$10 nm). Ainsi, la protéine induit une diminution de la vitesse de dissolution à $E_{\text{corr}}$ et, par conséquent, une diminution de la quantité de Cu$_2$O redéposé et de l’épaisseur de la couche oxydée.

Mots clés : Alliage de cuivre / eau de mer / adsorption de protéine / EIS / XPS / ToF-SIMS

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1 Introduction

Power plants require cooling circuits with water as the cooling agent; therefore, they are generally located on seacoasts owing to the ready availability of abundant seawater. Tubes are the basic components of heat exchangers; they provide the heat transfer surface between one fluid flowing inside the tubes and other fluid flowing outside the tubes [1]. In cooling circuits, the water is usually circulating but some parts inside the tubes where water is stagnant may be found, depending also on operation time; therefore, hydrodynamics is one of the parameters to be studied.

Copper and copper alloys are commonly used in condensers and heat exchangers due to their high thermal conductivity, good resistance to corrosion and good mechanical workability. Cu-Ni alloys are preferred in marine environments because of their corrosion resistance due to the formation of a thin, adherent, protective surface film which forms naturally and quickly upon exposure to clean seawater. That surface film is complex and predominantly made up of cuprous oxide, often containing nickel and iron oxides, cuprous hydroxychloride and cupric oxide [2].

Cooling circuits of industrial plants are ideal incubators for microorganisms because they offer plenty of water, are maintained at temperatures between 30 °C to 60°, at pH of 6 to 9, have good aeriation and provide a continuous source of nutrients, such as inorganic or organic compounds. The microorganisms present in cooling water circuits can be divided into planktonic or sessile cells. Sessile ones attach to surfaces and form what is known as biofilm. The development of a biofilm is considered to be a multistage process involving the following major steps: (a) formation of an organic conditioned film on the solid surface by adsorption of biomolecules such as proteins [3]; (b) transport of microorganisms from the water to the surface; (c) adhesion of microorganisms onto the surface; (d) replication of the attached cells and production of exopolymers; (e) detachment of parts of the biofilm that are swept along by the flowing water to repeat the process of biofilm formation elsewhere [4]. Biofouling is a consequence of biofilm formation; the significant negative effects of biofouling are the blockage of water free flow in the cooling circuit and consequent mechanical damage to pumps, clogging of condenser tubes, reduction of the heat transfer efficiency and microbially induced corrosion (MIC) also called biocorrosion [5]. Cu-Ni alloys have also shown good resistance to biofouling; the reason for the antifouling behaviour of these alloys is still not fully understood but the protective surface film should play a role [6].

There are two opposite goals for the control of microbial adhesion and biofilm formation: one is the prevention of biofilms, and the other one is their promotion. Controlling the adsorption of biomolecules, which is the first step in biofilm formation, by modifying the surface properties of the material may represent a good strategy for inhibiting microbial growth [7]. The global objective of this work was to study the influence of biomolecules adsorption on the electrochemical behaviour of 70Cu-30Ni (wt. %) alloy and the chemical composition of oxide layers, in different hydrodynamics conditions (i) stagnant conditions; (ii) under flow and stirring of the solution; and (iii) using a rotating ring electrode. In this work, the chosen biomolecule was the bovine serum albumin (BSA), a model protein often used to study the protein-surface interactions due to its low cost and to a good knowledge of its properties [8,9]. Electrochemical measurements (corrosion potential ($E_{corr}$) vs. time, polarization curves and electrochemical impedance spectroscopy (EIS)) performed in static artificial seawater (ASW) during the very first steps of oxide layers formation (1 h immersion time) were combined to surface analyses by X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS).

2 Experimental

2.1 Samples and solution

The samples provided by RSE S.p.A. were cut from real condenser tubes, and then flattened at Chimie ParisTech. Before each experiment, samples were mechanically polished with SiC papers down to grade 1200, then degreased in an ultrasonic bath three times in acetone for 5 min, once in ethanol for 10 min, and once in water for 10 min, dried under an argon flow, and finally exposed to UV for 15 min.

The solution under study was aerated artificial seawater (ASW; composition (g/L): NaCl (24.615), KCl (0.783), Na₂SO₄ (6.150), MgCl₂(H₂O)₆ (11.060), CaCl₂ (1.16), NaHCO₃ (0.201); pH = 8.0; ionic strength = 0.7155 M), without and with 20 mg.L⁻¹ of BSA.

2.2 Electrochemical measurements

The electrochemical measurements were performed with a three-electrode cell, designed and manufactured at Chimie ParisTech, with the material to be studied (70Cu-30Ni alloy) as the working electrode, a platinum wire as the counter-electrode, and a saturated calomel electrode (SCE) as the reference electrode. Experiments were carried out at room temperature and in stagnant conditions (static working electrode and solution).

The corrosion potential ($E_{corr}$) was followed during the first hour of immersion, then cathodic or anodic polarization curve was plotted separately starting from +20 or −20 mV vs. $E_{corr}$, respectively, using a scan rate of 0.5 mV.s⁻¹. Electrochemical impedance diagrams were plotted at $E_{corr}$ after 1 h of immersion, with a frequency domain ranging from $10^2$ to $10^4$ Hz, 7 points per decade, and an amplitude of 10 mV peak-to-peak. Electrochemical measurements were collected by means of an EC-Lab SP-200 system from Bio-Logic.
2.3 Surface analyses

Three 70Cu-30Ni samples were analyzed by XPS then by ToF-SIMS: (1) after polishing; (2) after 1 h of immersion at $E_{\text{corr}}$ in ASW without BSA; and (3) after 1 h of immersion at $E_{\text{corr}}$ in ASW with BSA. After the electrochemical measurements, the samples were gently dipped in ultra-pure water three times to remove the BSA molecules loosely bound to the surface, then dried with nitrogen before introduction in the fast-entry lock chamber of the XPS spectrometer.

XPS analyses were performed with a Thermo Electron Escalab 250 spectrometer, using a monochromatised Al Kα X-ray source (1486.6 eV). The analyser pass energy was 100 eV for survey spectra and 20 eV for high resolution spectra. The spectrometer was calibrated using Au 4f7/2 at 84.1 eV. The following core levels were recorded: Cu 2p (and Auger lines), Ni 2p, O 1s, C 1s, and N 1s. All spectra were referred to the C 1s peak for the carbon involved in C-C and C-H bonds, located at 285 eV. The fitting of the complex C 1s signal was based on some published data [10]. Curve fitting of the spectra was performed with the Thermo Electron software “Avantage”. The inelastic mean free path values were calculated by the TPP2M formula [11], and the photoemission cross-sections were taken from Scofield [12].

ToF-SIMS analyses were acquired using a ToF-SIMS V spectrometer (ION-TOF GmbH). The analysis chamber was maintained at less than $10^{-9}$ Pa in operation conditions. The depth profiles were performed using the instrument in dual beam mode. A pulsed 25 keV Bi+ primary ion source (LMIG) at a current of 1.2 pA (high mass resolution mode), rastered over a scan area of $100 \times 100 \mu m^2$, was used as the analysis beam. The sputtering was performed using a 1 keV Cs+ ion beam at a current of 50 nA, and rastered over an area of $300 \times 300 \mu m^2$. The depth profiles were obtained in negative polarity meaning only negative ions were analysed. The distribution of the ionized fragments, all measured simultaneously, were plotted versus Cs+ sputtering time. The intensity was reported using a logarithmic scale, which gave equal emphasis to signals of all intensities. The variation of the ion intensity with sputtering time reflects the variation of the in-depth concentration but is also dependent on the matrix from which the ions are emitted. Data acquisition and processing were performed using the IonSpec software.

3 Results

3.1 Electrochemical measurements

During the first hour of immersion, the corrosion potential $E_{\text{corr}}$ decreases till reaching a steady-state value of $-0.23 \pm 0.01$ V vs. SCE without BSA. The presence of 20 mg.L$^{-1}$ of BSA induces a more anodic $E_{\text{corr}}$ value ($-0.20 \pm 0.01$ V vs. SCE i.e. difference of $\sim$0.03 V with the value found without protein). Figure 1a shows the cathodic polarization curves obtained without and with 20 mg.L$^{-1}$ of BSA. The wide plateau observed for potentials ranging from $-0.40$ to $-1.00$ V vs. SCE illustrates the reduction of dissolved oxygen:

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^- \quad \text{at pH 8.0} \quad (1)$$

The corresponding current density is divided by 2 in the presence of the protein ($|j| \sim 40 \mu A.cm^{-2}$ without BSA to be compared to $|j| \sim 20 \mu A.cm^{-2}$ with BSA). This difference in plateau current is not necessarily due to the BSA but may also be induced by a difference in natural convection.

The short current plateau observed between $-0.25$ and $-0.30$ V vs. SCE ($|j| \sim 10 \mu A.cm^{-2}$) may illustrate the
first step of dissolved oxygen reduction with production
of H$_2$O$_2$ [13,14]:

$$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^- \text{ at pH 8.0} \quad (2)$$

The anodic polarization curves obtained without and with
20 mg.L$^{-1}$ of BSA are presented in Figure 1b. In the ab-
sence of protein, the anodic polarization curves show very
high dissolution currents. In particular, a pseudo-plateau,
corresponding to a current density of $\sim 2.5$ mA.cm$^{-2}$,c a n
be observed between 0.30 and 0.50 V vs. SCE; therefore,
this plateau current is not a passive current, and hence
the oxide film formed on the surface is not a passive layer.
Moreover, visual observation of the electrode surface after
an anodic scan shows a green layer, the thickness of which
increases with the end anodic potential. This green layer
corresponding to high anodic currents may be formed by
rededposition due to the saturation of the solution in cop-
per ions. No influence of the BSA on the anodic electro-
chemical behaviour can be seen. However, after the anodic
polarization curve, the green color is no more observed for
the alloy surface in the presence of BSA.

Figure 2a shows the impedance diagrams in the com-
plex plane plotted at $E_{corr}$ after 1 h of immersion in aerated artificial seawater, without protein and with BSA. The diagrams exhibit two capacitive loops: one high frequency (HF) depressed semi-circle, and a low frequency (LF) loop forming an angle of $\sim 45 ^\circ$ C with the X-axis that illustrates mass transport (Warburg-like impedance). The size of the HF loop is slightly in-
creased in the presence of BSA.

In Figure 2b, the imaginary part of the impedance ($Z_j$) is plotted as a function of the frequency ($f$) in log-
arithmetic coordinates. In the HF range, a straight line
with a slope lower than 1 in absolute value can be
observed, evidencing a constant-phase-element (CPE) beh-
vior. The impedance of a CPE is given by:

$$Z_{CPE}(\omega) = \frac{1}{Q(j\omega)^\alpha} \quad (3)$$

with $\omega = 2\pi f$. The CPE parameters $\alpha$ and $Q$ can be ob-
tained from the graphical methods presented by Orazem
et al. [15]. The parameter $\alpha$ is calculated from the slope
of the log $|Z_j|$ vs. log $f$ curve:

$$\alpha = \frac{\left| \frac{d \log |Z_j(f)|}{d \log f} \right|}{(4)}$$

and $Q$ is obtained from:

$$Q = \frac{1}{Z_j(f)(2\pi f)\alpha} \times \sin \left( \frac{\alpha \pi}{2} \right). \quad (5)$$

The parameters $\alpha$ and $Q$ obtained by graphical evalua-
tion of equations (4) and (5) are the same as would be
obtained by regression analysis. The $\alpha$ and $Q$ values for the impedance diagrams shown in Figure 2 are given in Table 1.

If this CPE behavior is assumed to be associated with
surface distributed time constants for charge-transfer re-
actions (time-constant distribution along the electrode
surface), then it is possible to apply the equation derived
by Brug et al. to calculate the effective capacitance asso-
ciated with the CPE [16,17]:

$$C_{eff} = Q^{1/\alpha} \left( R_e^{-1} + R_t^{-1} \right)^{(\alpha-1)/\alpha} \quad (6)$$

where $R_e$ is the electrolyte resistance and $R_t$ the charge
transfer resistance. The capacitance values extracted from
the impedance diagrams shown in Figure 2, of the order
Tableau 1. Paramètres CPE extraits par analyse graphique des diagrammes d’impédance présentés sur la figure 2 (Éqs. (4) et (5)) [15], résistances d’électrolyte et de transfert de charge estimées par ajustement de la boucle HF par le circuit équivalent et capacitance équivalente associée au CPE calculée à partir de l’équation (6).

<table>
<thead>
<tr>
<th>Without BSA</th>
<th>With BSA</th>
</tr>
</thead>
<tbody>
<tr>
<td>α</td>
<td>0.82</td>
</tr>
<tr>
<td>Q/F.cm(^{-2})</td>
<td>1.67 × 10(^{-04})</td>
</tr>
<tr>
<td>R_e/Ω.cm(^{2})</td>
<td>12.0</td>
</tr>
<tr>
<td>R_i/Ω.cm(^{2})</td>
<td>1197</td>
</tr>
<tr>
<td>C_off/F.cm(^{-2})</td>
<td>43 × 10(^{-06})</td>
</tr>
</tbody>
</table>

Fig. 3. (a) Spectres XPS des niveaux de cœur Cu 2p et (b) raie Auger Cu L\(^{3}\)M\(^{3}\)M\(^{4}\) pour 70Cu-30Ni après 1 h d’immersion à \(E_{\text{corr}}\) en eau de mer artificielle aérée sans et avec 20 mg.L\(^{-1}\) de BSA.

of several tens of μF.cm\(^{-2}\) (Tab. 1), are typical of those for a double layer capacitance (C_{dl}). Hence, the HF loop illustrates charge transfer and can be represented by the \(R_t/\Omega.CPE_{dl}\) equivalent circuit; its diameter is equal to \(R_t\).

In the presence of BSA, \(R_t\) is 1.4 times higher than without protein. This indicates that albumin leads to a decrease of the corrosion current (inversely proportional to \(R_t\)), and hence of the corrosion rate.

3.2 Surface analyses

For the sample after polishing, it is observed from XPS and ToF-SIMS data (not shown here) a mixed copper oxides (Cu\(_2\)O and CuO) and nickel hydroxide (Ni(OH)\(_2\)) layer, with a thickness of \(\sim 1.3\) nm and the following atomic composition: 43 at. % Cu\(_2\)O + 25 at. % CuO + 32 at. % Ni(OH)\(_2\). An enrichment in copper of the alloy enters the second region that extends up to 200 s of sputtering (Fig. 4) [19]. The atomic composition of this oxide film calculated from XPS data (93 at. % Cu\(_2\)O + 7 at. % Ni(OH)\(_2\)) indicates a Cu\(_2\)O-rich layer. It is important to mention that the depth analyzed by XPS is about 10 nm.

From the XPS Ni 2p\(_{3/2}\) core level spectrum with a peak located at 856.1 eV and the corresponding satellite at 861.7 eV, the presence of Ni(OH)\(_2\) in the surface layer is shown (Fig. 4) [19]. The atomic composition of this oxide film calculated from XPS data (93 at. % Cu\(_2\)O + 7 at. % Ni(OH)\(_2\)) indicates a Cu\(_2\)O-rich layer. It is important to mention that the depth analyzed by XPS is about 10 nm.

A characteristic ToF-SIMS negative depth profile obtained with 70Cu-30Ni alloy immersed during 1 h at \(E_{\text{corr}}\) in ASW without BSA is presented in Figure 5. This profile allows evidencing a possible stratification of the different compounds on the alloy surface. It shows four regions. A first one that extends from 0 s to 10 s of sputtering characterized by an increase of all signals and corresponding to the time necessary to reach a steady state. After 10 s, one enters the second region that extends up to 200 s of sputtering. This region is characterized by an intense CuO\(_2\) signal. As soon as one probes deeper into this region, a progressive increase of the NiO\(_2\) signal is observed. This indicates that the outer surface layer is mainly composed of copper oxide, with the presence of some Ni oxide and/or hydroxide, in agreement with XPS data. In the third region that extends from 200 s to 290 s, a sharp decrease of a binding energy of 570.2 eV (Fig. 3b) demonstrate only the presence of Cu\(^{2+}\) (no Cu\(^{2+}\) as for the sample after polishing) [18].
Fig. 4. Spectres XPS des niveaux de cœur Ni 2p pour 70Cu-30Ni après 1 h d’immersion à $E_{corr}$ en eau de mer artificielle aérée sans et avec 20 mg.L$^{-1}$ de BSA.

the CuO$_2^-$ signal and a very intense NiO$_2^-$ signal are observed. This region is assigned to the formation of a nickel oxide and/or hydroxide inner layer in which the presence of oxidized copper cannot be excluded. Finally, after 290 s of sputtering, one enters the fourth region characterized by a sharp decrease of all oxidized signals (180°, CuO$_2^-$ and NiO$_2^-$) and a constant and intense plateau for the Ni$_2$ signal that is characteristic of the metallic substrate.

From the ToF-SIMS depth profiles, it can be concluded that the absence of BSA on the alloy surface can be observed: a 18 nm-thick outer layer mainly composed of copper oxide and a 12 nm-thick inner layer mainly composed of nickel oxide and/or hydroxide, with a global thickness of $\sim$ 30 nm. To convert a sputtering time into an oxide layer thickness, the theoretical sputtering rates of pure metallic Cu and Ni weighted by the fractions of the two elements in the alloy (i.e. sputtering rate of Cu+Ni oxide = 0.7 x sputtering rate of metallic Cu + 0.3 x sputtering rate of metallic Ni).

The N 1s spectrum recorded after immersion in ASW with BSA (Fig. 6a) exhibits a major symmetric peak, centered at 400.2 eV, as expected for the amine or amide groups of BSA [20]. The C 1s signal obtained in the same conditions is shown in Figure 6b. It can be fitted with three contributions corresponding to well identified carbon bonds present in the BSA molecule: C1, at a binding energy of 285.0 eV, assigned to C-C and C-H; C2, at a binding energy of 286.4 eV, attributed to C-N and C-O single bonds; and C3, at a binding energy of 288.3 eV, assigned to O=C-O and O=C-N (peptide bonds) bonds [10].

From the N 1s and C 1s signals, it is possible to calculate different “nitrogen-carbon” or “carbon-carbon” atomic ratios. The values of these ratios obtained for the 70Cu-30Ni alloy immersed in ASW without and with BSA, as well as those estimated in previous studies for the BSA powder [10, 21] are presented in Table 2. The good agreement between the values for the sample put into contact with the BSA and the BSA powder provides a fingerprint for the protein, and allows us to conclude that the protein is present on the surface. The thickness estimated from XPS data for this adsorbed layer is $\sim$ 3 nm, which corresponds to one monolayer [9].

4 Discussion

After short-term immersion (1 h of exposure) at $E_{corr}$ in ASW without BSA, combined XPS and ToF-SIMS data show two oxidized layers: an outer layer mainly composed of cuprous oxide (Cu$_2$O) and an inner layer mainly composed of oxidized nickel. Thus, the surface layers can be depicted by the model presented in Figure 7a. The presence of BSA leads to a mixed oxide layer composed of CuO, Cu$_2$O, and Ni(OH)$_2$ (Fig. 7b). Compared to the results obtained without BSA, there is a marked decrease of the Cu$_2$O content in the oxide layer, and its thickness is lower ($\sim$ 10 nm).

On the other hand, impedance diagrams exhibit a LF loop illustrating mass transport (diffusion convection...
Fig. 5. Characteristic ToF-SIMS negative depth profile of 70Cu-30Ni after 1 h of immersion at $E_{\text{corr}}$ in aerated artificial seawater without BSA.

Fig. 5. Profils ToF-SIMS en mode négatif de 70Cu-30Ni après 1 h d’immersion à $E_{\text{corr}}$ en eau de mer artificielle aérée sans BSA.

Table 2. Atomic ratios calculated from the XPS N 1s and C 1s core level spectra recorded for the BSA powder, and for 70Cu-30Ni after 1 h of immersion at $E_{\text{corr}}$ in aerated artificial seawater without and with 20 mg.L$^{-1}$ of BSA.

<table>
<thead>
<tr>
<th></th>
<th>N/Total</th>
<th>N/(C2+C3)</th>
<th>C1/Total</th>
<th>C2/Total</th>
<th>C3/Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSA powder</td>
<td>0.22</td>
<td>0.48</td>
<td>0.54</td>
<td>0.26</td>
<td>0.20</td>
</tr>
<tr>
<td>ASW</td>
<td>0.03</td>
<td>0.14</td>
<td>0.78</td>
<td>0.13</td>
<td>0.09</td>
</tr>
<tr>
<td>ASW+BSA</td>
<td>0.20</td>
<td>0.45</td>
<td>0.56</td>
<td>0.22</td>
<td>0.22</td>
</tr>
</tbody>
</table>
Fig. 7. Models of the surface layers deduced from combined XPS and ToF-SIMS results for 70Cu-30Ni after 1 h of immersion at $E_{corr}$ in aerated artificial seawater (a) without and (b) with 20 mg.L$^{-1}$ of BSA.

Fig. 7. Modèles des couches de surface déduits de la combinaison des résultats XPS et ToF-SIMS pour 70Cu-30Ni après 1 h d’immersion à $E_{corr}$ en eau de mer artificielle aérée (a) sans et (b) avec 20 mg.L$^{-1}$ de BSA.

impedance) and show lower corrosion current in the presence of the protein.

It is accepted by many authors that the corrosion of copper alloys is controlled by mass transport processes to and from corroding surfaces, involving $O_2$, $Cl^-$, $OH^-$, $Cu^+$ and $CuCl_2^-$ species [22]. The anodic reactions involve:

$$Cu \rightarrow Cu^+ + e^- (7)$$

followed by the formation of the cuprous complex:

$$Cu^+ + 2Cl^- \rightarrow CuCl_2^- (8)$$

Then, cuprous oxide can be formed from $CuCl_2^-$ as follows [13]:

$$2CuCl_2^- + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^- (9)$$

Moreover, there are basically two mechanisms of de-alloying for binary alloys proposed in the literature [13]:

1. simultaneous dissolution of both components of the alloy followed by redeposition of one component (usually the more noble one);
2. selective dissolution of one element from the alloy.

Beccaria and Crousier studied the de-alloying of Cu-Ni alloys exposed to natural seawater for 660 h and found simultaneous dissolution of both components with possible redeposition of copper for nickel contents lower than 50%, whereas for nickel concentrations higher than 50% selective dissolution of copper took place [23]. Results obtained by Mansfeld et al. for long-term exposure (1–3 months) to natural seawater suggest that de-alloying of 70Cu-30Ni is initially due to simultaneous dissolution of copper and nickel and subsequent redeposition of copper in agreement with the results of Beccaria and Crousier [13].

Our results obtained for short-term exposure to ASW are in agreement with the conclusions drawn by Beccaria and Crousier, and Mansfeld et al.; the cuprous oxide $Cu_2O$ detected on the surface by XPS and ToF-SIMS is formed by redeposition of dissolved copper.

The combination of electrochemical measurements and surface analyses allows us to conclude that in stagnant conditions the BSA leads to a decrease of the dissolution rate at $E_{corr}$ and hence a decrease of the amount of redeposited $Cu_2O$ and of the oxide layer thickness.

5 Conclusions

The influence of BSA adsorption on the electrochemical behavior of 70Cu-30Ni alloy and the chemical composition of oxide layers was studied in static artificial seawater by combined electrochemical measurements and surface analyses.

From polarization curves, high anodic dissolution currents were shown (no passive current). The BSA had a slight effect on the electrochemical behavior of the copper alloy. Thus, $E_{corr}$ value after 1 h of immersion was $\sim$30 mV more anodic with BSA, and EIS measurements indicated a decrease of the corrosion current induced by the protein.

From XPS and ToF-SIMS analyses, different surface chemical compositions of 70Cu-30Ni were shown without and with BSA. In the absence of BSA, two oxidized layers were observed: an outer layer mainly composed of copper oxide ($Cu_2O$ redeposited layer) and an inner layer mainly composed of oxidized nickel, with a global thickness of $\sim$30 nm. In the presence of BSA, the protein was detected on the surface and the thickness of the adsorbed layer was $\sim$3 nm, corresponding to one monolayer. The presence of BSA led to a mixed oxide layer ($CuO$, $Cu_2O$, Ni(OH)$_2$) with a lower thickness ($\sim$10 nm).

The combination of electrochemical measurements and surface analyses allows us to conclude that the BSA
induces a decrease of the dissolution rate at $E_{\text{corr}}$ and hence a decrease of the amount of redeposited Cu$_2$O and of the oxide layer thickness.

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