

Article

Effect of the Annealing Treatment on the Microstructure and Corrosion Resistance of a Cu-Al-Ni Alloy

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Abstract: The influence of annealing treatment on the microstructure and the corrosion behaviour of a complex bronze Al-Ni alloy was analysed. The microstructural characterization after thermic treatment shows that the retained β -phase disappears and the K_{II} -phase undergoes a spheroidization process. Moreover, there is an augmentation of K-phase precipitates within the α -phase, particularly K_{IV} and K_V , which homogenizes the distribution of alloying elements between the phases. The corrosion behaviour was investigated by means of selective corrosion tests, potentiodynamic measurements, and electrochemical impedance spectroscopy. All of the experiments showed that thermic treatment greatly improves the corrosion resistance of the alloy. As such, annealing treatment influences a microstructure to be more dealloying resistant, which allows the development of a more protective air-formed passive film. On the other hand, the lower current registered after anodic peaks and Electrochemical Impedance Spectroscopy data seem be correlated with a more protective layer formed on annealed material. As such, this protective character is due to a greater incorporation of Al^{3+} , Ni^{2+} and Cu^{2+} in the passive film, as revealed by X-ray Photoelectron Spectroscopy results.

Keywords: copper alloy; EIS; dealloying corrosion; XPS; cyclic voltammetry



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1. Introduction

Nickel aluminium bronze alloys have been developed to produce materials with better properties than pure copper for specific purposes [1]. Among Cu-based alloys, aluminium bronzes are used extensively, because they possess superior properties such as high strength, low corrosion susceptibility, and wear and impact resistance [2]. Bronzes alloyed with about 10% in weight of aluminium show an optimal compromise between mechanical properties and corrosion resistance. Furthermore, small quantities of Fe and Ni may be added to aluminium bronzes to modify their mechanical properties and corrosion resistance [3,4]. Bronze aluminium alloys containing between 8 wt.% and 14 wt.% aluminium and approximately 2 to 4 wt.% nickel and iron [5] are the most widely used, especially for propulsion and seawater handling systems. These alloys are metallurgical complex materials, in which small variations in composition can result in the development of markedly different microstructures, which turn into large variations in properties [6].

Generally, these alloys are employed in an “as-cast” condition, but in the literature there are recommendations to improve their properties by submitting them to different thermal treatments. Their phase transformations and mechanical behaviour as a consequence of the heat treatments have been studied widely, but the effect of heat treatment on the corrosion resistance of these materials is not fully understood [7–9]. It is known that some treatments can improve the mechanical properties but make the corrosion resistance worse. Therefore, a trade-off between mechanical properties and corrosion resistance should be considered in the thermal treatment design.

The aim of this work is to study the influence of a heat treatment (annealing) in the corrosion resistance of a complex aluminium bronze in a chloride-containing environment. The goal is to explore the influence of the microstructural changes in the properties and/or

composition of the passivation layer developed at their surface, and to clarify the mechanisms of the corrosion processes involved. For this purpose, characterization techniques such as X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) and optical microscopy (OM) were combined with electrochemical techniques such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). Furthermore, the dealloying corrosion resistance of these materials was studied according to the standard test for the dealloying of brasses.

2. Materials and Methods

2.1. Preparation of the Samples

The nominal chemical composition of the aluminium bronze alloy employed (supplied by Fundivisa, Vilagarcía de Arousa, Spain) is presented in Table 1.

Table 1. Chemical composition in wt.% of the material used in this study.

Element	Cu	Al	Ni	Fe	Mn	Si	Zn	Others
wt.%	78.86	8.34	4.77	4.79	1.17	0.13	1.89	0.046

The experimental parameters for annealing were 675° (± 10 °C) for 2 h followed by air cooling, according to the ASTM B148 procedure. The annealed samples were designated as “BR”, and the “as cast” material was identified as “B”.

Specimens of 2.5 cm $\times$ 2.5 cm $\times$ 0.2 cm were cut and prepared for characterization as follows: first, they were abraded with SiC-sand paper (Struers, Copenhagen, Dinamarca) starting from 220 grit, and then sequentially with 500-, 1200- and 2400-grit grades. Finally, the samples were polished with diamond paste from 9 down to 1 μ m, and finished to 0.04 μ m with colloidal SiO₂ (Struers, Copenhagen, Dinamarca).

2.2. Metallographic Characterization

The microstructure was examined using optical microscopy (OM) employing an Olympus GX51 equipped with an image analysis program (Olympus Analysis Five, Hamburg, Germany) and scanning electron microscopy (SEM) using a JEOL 5410 (Tokyo, Japan), equipped with energy dispersive X-ray spectroscopy (EDX). Prior to the microstructural characterization, the samples were etched in a FeCl₃-HCl-ethanol solution (Scharlab, Barcelona, España).

2.3. Evaluation of the Resistance to Dealloying

The resistance of the materials to dealloying was studied according to the UNE-EN ISO 6509 standard test for the dealloying of brasses. The test consists in a microscopic study of the dealloyed layer after exposure to 1 wt.% CuCl₂ solution. The surface tested was 2 cm², delimited using an O-ring bearing cell in which the volume of the solution/metal surface ratio was 100 mL/cm². The evolution of the corrosion was monitored visually. At the end of the exposure, the samples were rinsed and dried. The exposed surface and cross sections were examined at the optical microscope. The depth of the attacked zones was measured using an image analysis program.

2.4. XPS Characterization

The chemical composition of the B (as cast) and BR (annealed) samples was examined “ex-situ” by XPS surface analysis. The survey spectra were recorded using a Thermo Scientific K-Alpha instrument (Waltham, MA, USA); they revealed C1s, O1s, N1s, Cu2p, Ni2p, and Al2s peaks. A monochromatic X-ray source Al K α (148.86 eV) was used for all of the samples and experiments. The X-ray monochromatic spot was 400 μ m in diameter, and the corresponding sampling area was 0.335 mm². The residual vacuum in the analysis chamber was maintained at around 3×10^{-9} mbar (3×10^{-7} Pa). Photoelectrons were collected from a take-off angle of 90° relative to the sample surface. The measurements

were performed in Constant Analyzer Energy mode (CAE) with 100 eV pass energy from the survey spectra and 20 eV pass energy for high resolution spectra.

The binding energies' (BEs) positions were referenced to the C1s photo peak at 285.0 eV (C1s hydrocarbon peak). An electron flood gun was also employed to minimize surface charging (charge compensation).

The atomic concentrations were determined from the XPS peak areas using the Shirley background subtraction technique and the Scofield sensitivity factors. The samples were fixed to the sample holder using a metallic clip to ensure the electrical conductivity.

2.5. Electrochemical Characterization

The electrochemical experiments were performed at room temperature in a conventional three-electrode all-glass cell, where the working electrode was the bronze aluminium alloy (0.28 cm² exposed area). A Pt mesh was used as a large-surface auxiliary electrode, and a saturated calomel electrode (SCE) was used as a reference. The employed solution was 3.5 wt.% NaCl solution (Scharlab, Barcelona, España). Electrochemical measurements (Potentiodynamic polarization, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy) were conducted using a potentiostat PGSTAT 30 Autolab (Ecochemie, Utrecht, The Netherlands). The polarizations were performed at 1 mVs^{−1} scan rate. The use of a low scan rate was chosen to give time enough for the relaxation of the redox processes occurring in the passive layer.

The EIS was recorded at the open circuit potential (OCP) from 1 MHz down to 1 mHz. The amplitude of the superimposed AC signal was 10 mV rms. In order to verify reproducibility, each experiment was carried out at least twice.

3. Results and Discussion

3.1. The Effect of Annealing on the Microstructure

The metallographic structure of the B (as-cast) and BR (annealed) samples is shown in Figure 1. The structure of the “as-cast” samples consists of light etched areas of the α -phase, which is an FCC Cu-rich solid solution; some retained β -phase; and several intermetallic phases, which are referred as the K-phase. The K_I phase is an iron-rich solid solution with a globular or rosette-shaped morphology. The K_{II} phase is also an iron-rich, rosette-shaped solid solution but of smaller size than the K_I phase, and distributed at the α boundary. The K_{III} phase appears at the α - β boundary forming α +K_{III} eutectic, and it is Ni rich. The K_{IV} phase represents an enrichment in Fe, and appears forming fine precipitates within the α -phase.

Annealing—the BR (annealed) condition—results in the elimination of the retained β -phase, the spheroidization of K_{III}, the increasing density of fine K_{IV}-phase precipitates in the α -phase, and the presence of K_V-phase precipitates in the α -phase, in the form of fine precipitates which are cylindrically shaped and rich in Ni and Al.

3.2. Dealloying Corrosion Analysis

The major corrosion problem encountered in bronze–aluminium alloys in seawater applications is dealloying corrosion. Dealloying is the selective dissolution of one element or phase in the material [10–12]. In the case of aluminium bronze alloys, aluminium is the preferentially dissolved element [13,14].

Dealloying in bronze–aluminium was studied according to the UNE-EN ISO 6509 standard test for the dealloying of brasses. The discussion focused on the most representative results obtained in samples exposed to the solution for 24h. The cross sections and the surfaces of the B (as-cast) and BR (annealed) tested samples are shown in Figures 2 and 3.

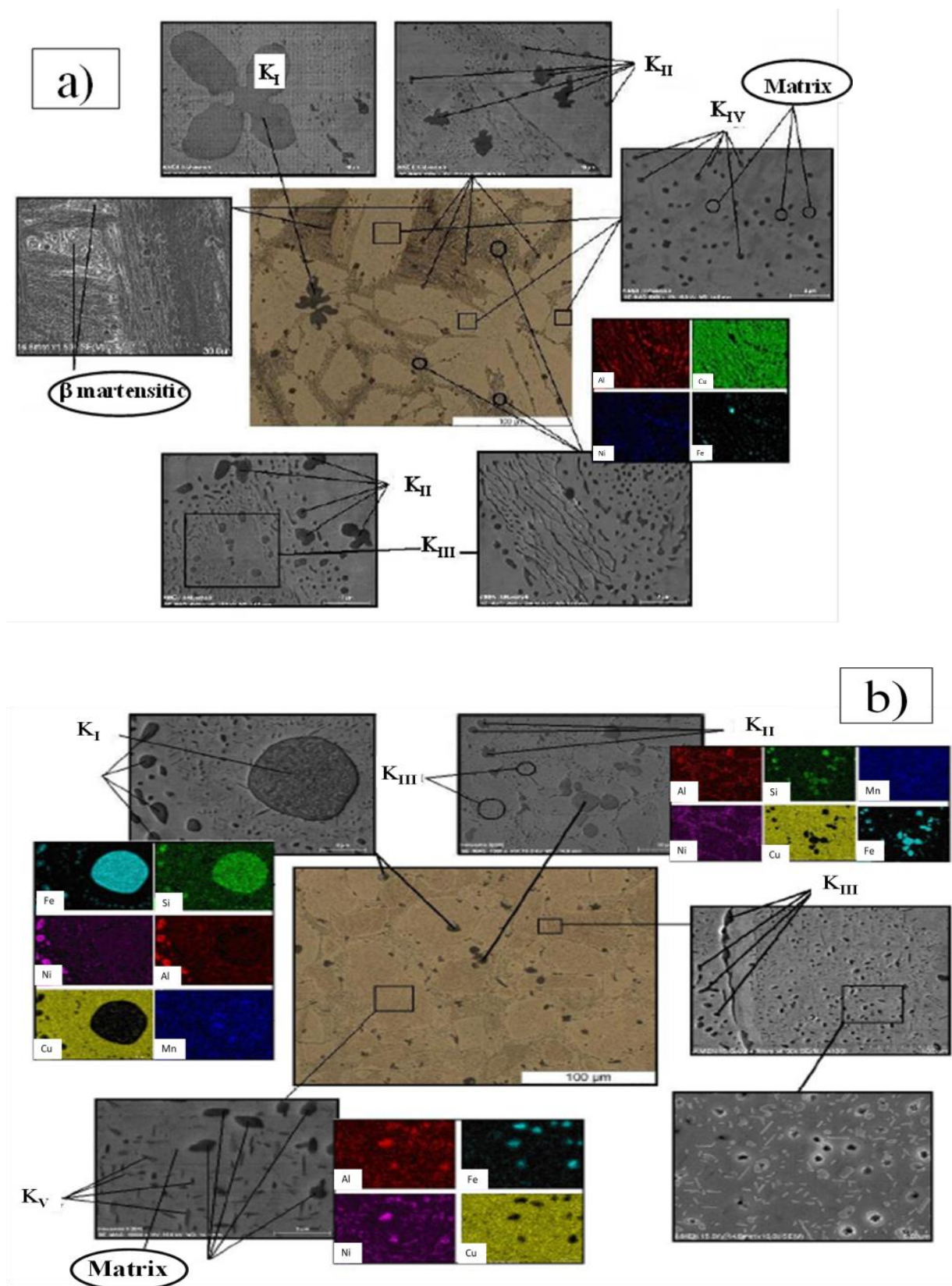


Figure 1. SEM image and phase identification of the (a) B (as-cast) samples and (b) BR (annealed) samples. See the text for details.

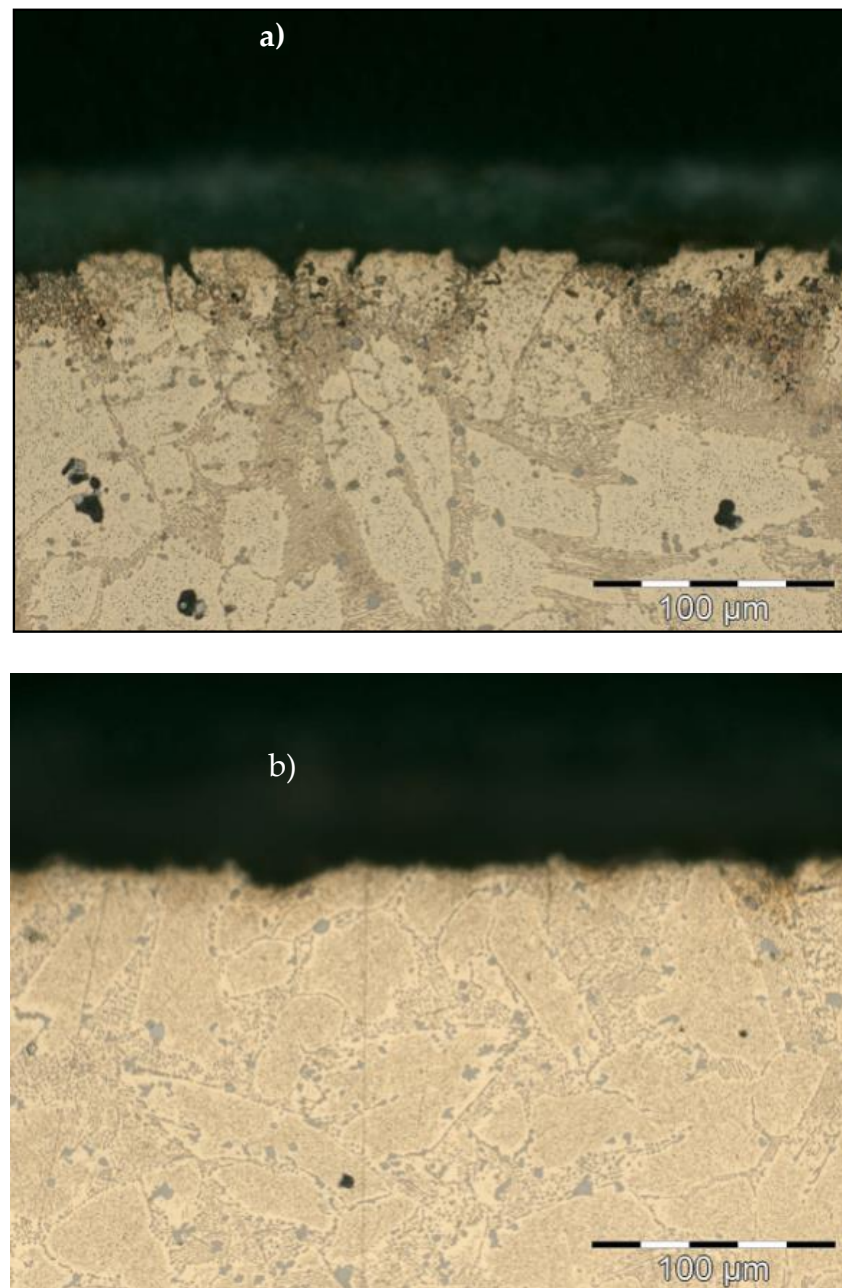


Figure 2. Cross section view after the dealloying test for (a) “as-cast” samples and (b) annealed samples.

After 24 h of immersion, intergranular corrosion is distinctly developed in both samples. As it can be observed in Figure 2a,b, the cross sections show that the attack is more intense, both in terms of pit depth and density of pits for the B (as-cast) samples than for the BR (annealed) samples. Moreover, the corrosion process in the BR (annealed) sample (Figure 3b) has just contoured the grains, while the attack has progressed beneath the surface for the B (as-cast) sample (Figure 3a).

The resistance for this type of corrosion is evaluated through the quantification of the average pit depth. The average corrosion depths of both materials obtained from the cross section images (Figure 2a,b) are shown in Table 2.

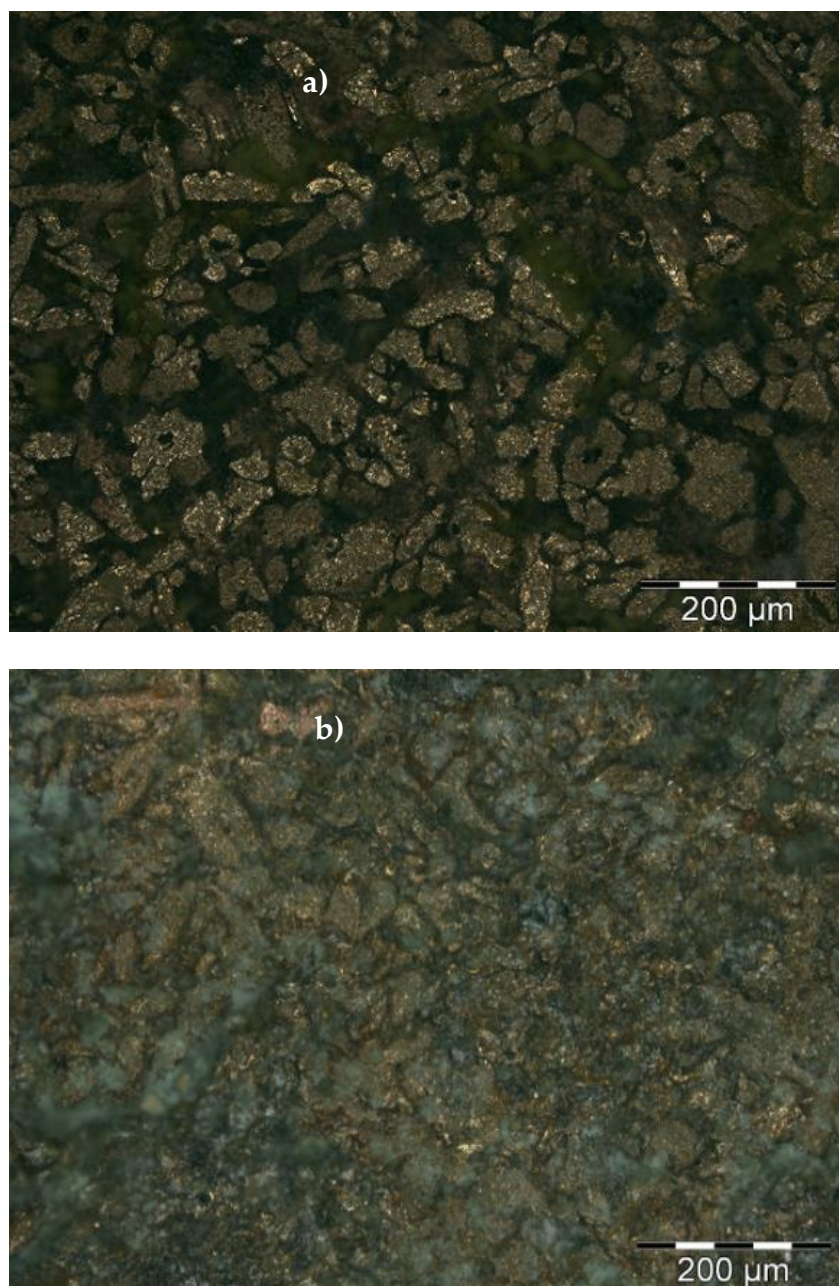


Figure 3. Surface aspect of the (a) “as-cast” samples and (b) annealed samples after the dealloying test.

Table 2. Average depths of the corroded zones measured in the cross sections of samples B (as cast) and BR (annealed) after the dealloying test.

Sample	Average Corrosion Depth of Pits (μm)
Sample B	60
Sample BR	20

The decrease of 66% in the average pit depth for BR (annealed) indicates that annealing markedly improves dealloying corrosion resistance.

In general, the dealloying corrosion of multi-phase copper alloys is reported [13] to be confined to the retained β and $\alpha+K_{III}$ phases. In the case of the retained β -phase, the selective dissolution was explained by galvanic coupling with the α -phase. As the retained β -phase is aluminium rich, at the corrosion potential it reaches a more anodic potential

than the α -phase, and undergoes selective dissolution. For (α +K_{III}) eutectoid, because the α -matrix (α +K_{III})/eutectoid interface is a small area with very high difference in alloying elements (Al, Fe, Ni), galvanic cells can be easily developed and dealloying corrosion resistance decreases.

Annealing treatment promotes a microstructure that is more dealloying resistant [14,15]. After annealing treatment, some observations can be noted: the retained β -phase disappears and the K_{III}-phase undergoes a spheroidization process. Moreover, there is an augmentation of K-phase precipitates within the α -phase, particularly K_{IV} and K_V, which homogenizes the distribution of alloying elements between the phases, as can be observed in Table 3. This fact decreases the difference of electrical potential and the number of sites available for galvanic coupling [15]. Furthermore, the more homogeneous distribution of the microconstituents in the BR (annealed) samples do not allow the formation of a continuous path for the penetration of the selective dissolution, which limits the corrosion depth to the near-surface layers exposed to the solution.

Table 3. Chemical composition of the phases for the B (as cast) and BR (annealed) samples (wt.%) obtained by EDX analysis.

Element	Sample B		Sample BR	
	α Phase	K _{III}	α Phase (BR)	K _{III} (BR)
Cu	84.5–85.6	30.9–43.0	76.23	28.68
Al	7.8–8.6	18.9–26.5	9.82	19.68
Ni	2.7–2.8	24.0–29.0	6.11	24.00
Fe	1.8–3.5	10.5–16.0	6.57	25.76

3.3. X-ray Photoelectron Spectroscopy Analysis

XPS measurements were used to determine the surface composition and chemical environment of the air-formed films on the B (as cast) and BR (annealed) samples. This is a useful technique to get a semi-quantitative approximation of the composition of the oxides formed on air. In order to create the chemical assignments, the deconvolution of the C1s spectra was performed and referenced to the main peak at 285 eV, which is assigned to the hydrocarbon peak.

Survey scans of the XPS spectra for the B (as-cast) and BR (annealed) samples show that the main elements on the air-formed layer are Cu, O, Ni and Al. The high-resolution spectra for those elements are depicted in Figure 4, employing the B sample.

The O1s signal was adjusted to one peak at 530.1 eV, and was assigned to O^{2−}.

The copper 2p level splits into two sublevels, 2p_{3/2} and 2p_{1/2}. The high-resolution spectrum of Cu 2p_{3/2} was resolved in two different peaks—Cu⁰ at 932.5 eV and Cu⁺ at 934.2 eV—and two satellite peaks at 943.8 and 946.9 eV. It is generally accepted that XPS can be used to distinguish between Cu metal, Cu₂O and CuO. CuO is characterized by the presence of a shake-up satellite at 9 eV higher binding energy than the main peak. In the Cu₂O spectrum, that satellite is not present.

The Ni 2p_{3/2} signal could be fitted with two peaks: one at 852.8 eV corresponding to the metallic state and another at 856.2 eV, which could be assigned to Ni²⁺, and a satellite peak at 862 eV. The Al2s signal is fitted to a peak at 119.2 eV assigned to Al³⁺.

The main components of the air-formed oxide layers for both materials are O^{2−}, Cu⁺, Cu²⁺, Al³⁺, and Ni²⁺. Table 4 presents the calculated atomic concentration of surface elements from the survey spectra.

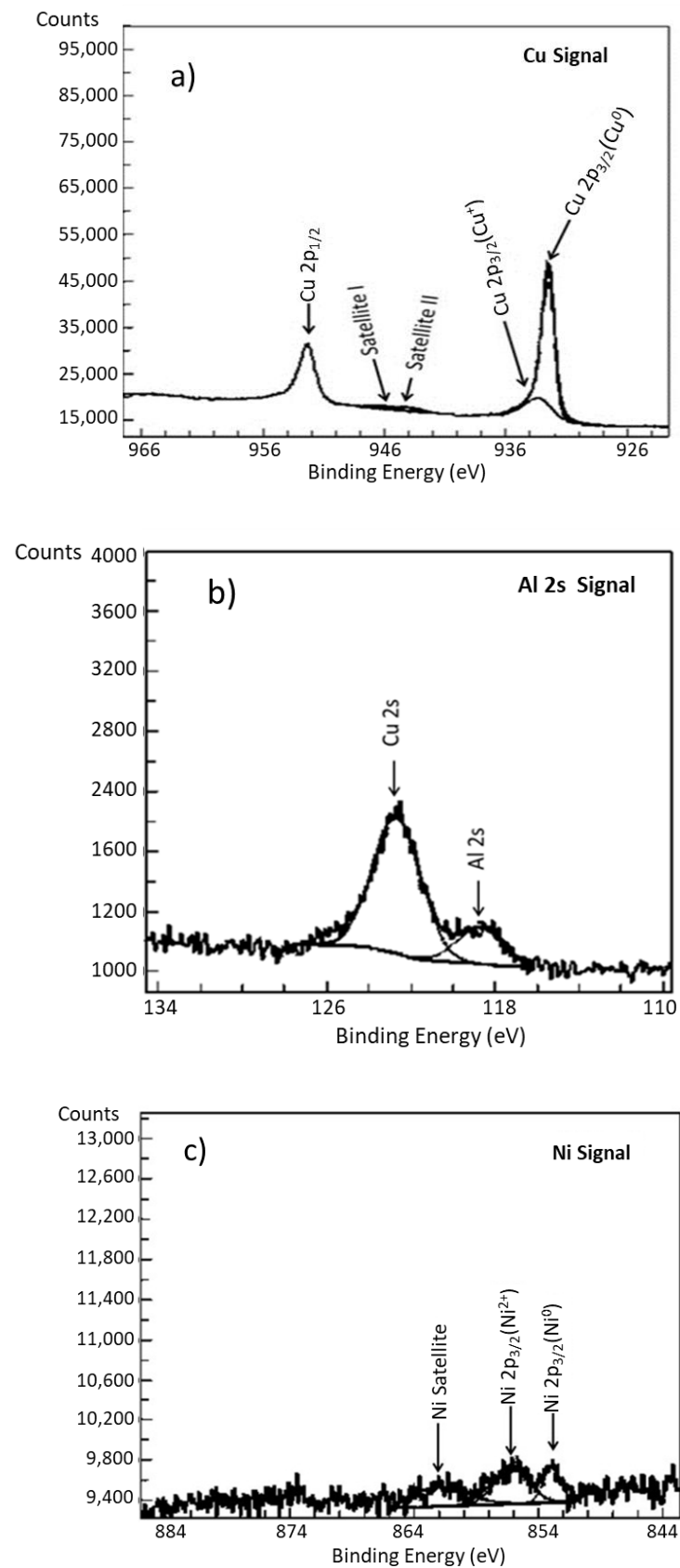


Figure 4. High-resolution XPS spectra of the native film for a B sample corresponding to the (a) Cu 2p and Cu 3s, (b) Al 2s and (c) Ni 2p spectra.

Table 4. Chemical elemental composition obtained from the XPS survey spectra in at.%.

Samples	O ^{2−}	Cu		Al ³⁺	Ni	
-	-	Cu/Cu ⁺	Cu ²⁺	-	Ni ⁰	Ni ²⁺
B	64.40	30.60	8.20	2.80	0.40	0.80
BR	70.50	23.40	11.50	3.80	0.43	1.46

The main difference observed between both materials concerns the quantification of different species. As such, the amount of Cu²⁺ in the BR (annealed) is higher than in B (as cast) sample, considering the contributions of the corresponding satellite peaks. On the other hand, the ratio of Cu/Al is slightly larger for the BR (annealed) samples than for B (as cast) samples. Nickel is present as Ni⁰ and as Ni²⁺, and the data indicated that there is more Ni²⁺ in the BR (annealed) samples than in the B (as-cast) samples.

From the XPS analysis, it can be concluded that the air-formed oxide layer is basically a Cu₂O-based oxide containing Ni²⁺ and Al³⁺ species, for both samples. The reported data indicate that annealing promotes a larger incorporation of Al³⁺, Ni²⁺ and Cu²⁺ to the oxide structure. The incorporation of Fe species was not detected.

3.4. Characterization of the Alloys by Cyclic Voltammetry

Figure 5 shows the cyclic voltammogram of the B (as-cast) and BR (annealed) samples in 3.5% NaCl solution, at pH 7.9. The potential scan started after a cathodic reduction of the native oxide layer at −1.5 V vs. SCE for 1 min.

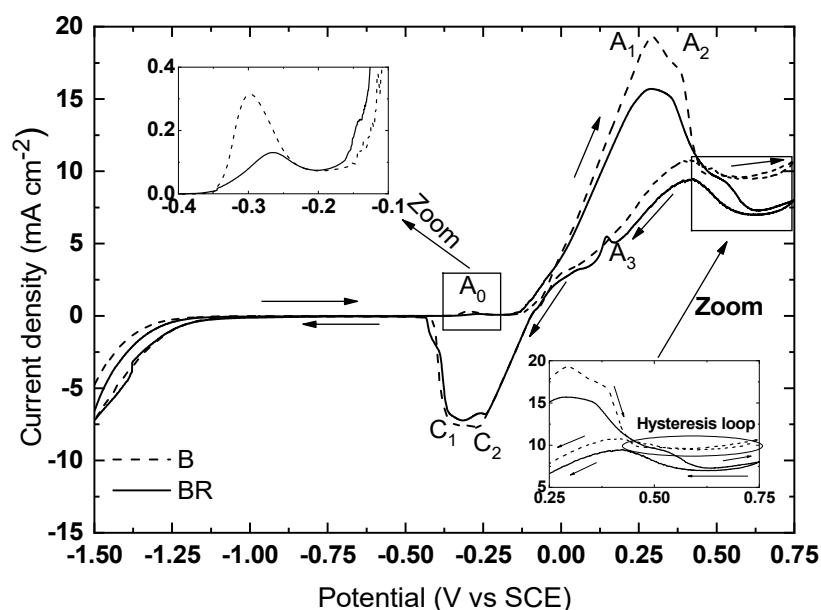


Figure 5. Cyclic voltammogram (from −1.5 to 0.75 V vs SCE) in 3.5 wt.% NaCl solution at a 1 mV s^{−1} scan rate for B (as-cast) and a BR (annealed) samples.

The cyclic voltammograms show well-defined oxidation and reduction peaks. As such, in the forward scan, three oxidation peaks (A₀, A₁ and A₂) were observed. A₀ appears at −0.25 V, and might be related with the Cu₂O formation. At more anodic potential values, two signals can be differentiated: A₁ (at +0.15 V) and A₂ (at +0.20 V). Both peaks could be related to the formation of CuCl₂ and CuO, respectively. In the reverse scan, two well-defined cathodic peaks were observed, C₂ and C₁, associated to reduction process of Cu ions.

The anodic sweep was reverted at different potentials with the aim to correlate the anodic and cathodic peaks. Two different measurements were carried out: in the first scan, the potential was reversed at 0 V (Figure 6), and in the second one, the potential

was reversed at +0.25 V (Figure 7). As can be seen in Figure 6, two reduction peaks were observed: C_0 and C_1 . The peak C_0 is missing in Figure 7, while a reduction peak, denoted as C_2 , appears at potential values which are more anodic than that of C_1 .

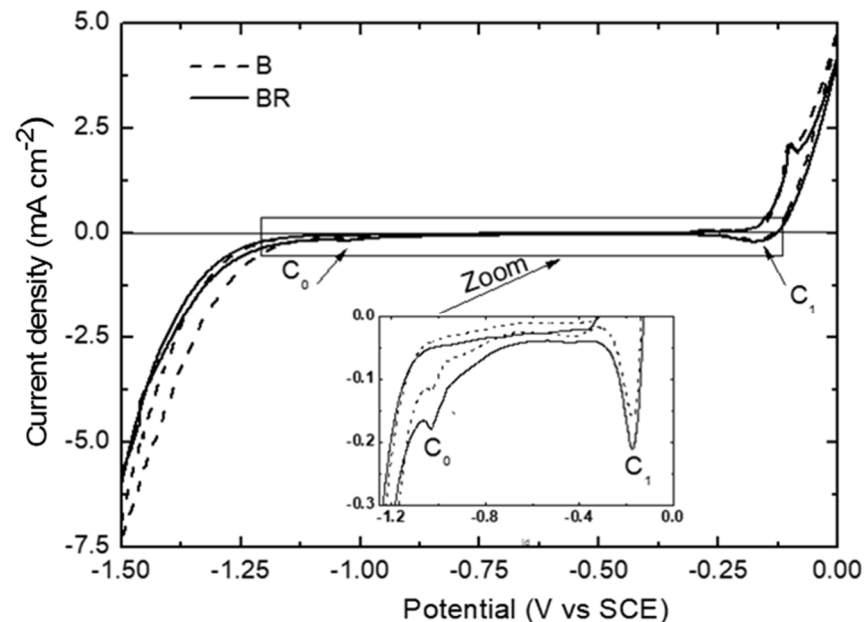


Figure 6. Cyclic voltammogram (from -1.5 to 0 V vs SCE) in 3.5 wt.% NaCl at a 1 mV s^{-1} scan rate for B and BR (annealed) samples.

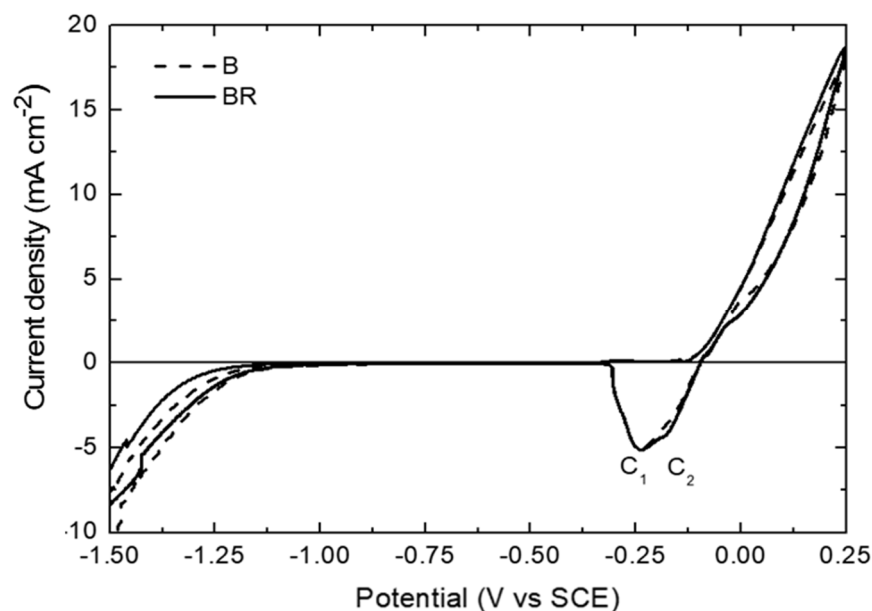


Figure 7. Cyclic voltammogram (from -1.5 to 0.25 V vs SCE) in 3.5 wt.% NaCl at a 1 mV s^{-1} scan rate for B (as cast) and BR (annealed) samples.

The presence of C_1 and C_2 peaks supports the assignment made previously. The disappearance of the C_0 peak can be justified, assuming that all of the Cu^+ formed at A_0 was oxidized at the more anodic potentials and reduced at the C_1 and C_2 peaks.

The equilibrium potentials for the $\text{Cu}_2\text{O}/\text{Cu}$ and CuCl/Cu redox processes at 25°C are given by Equations (1) and (2), respectively [16].

$$E_{\text{Cu}_2\text{O}/\text{Cu}} = 0.461 - 0.0591 \text{ pH} \quad (1)$$

$$E_{\text{CuCl/Cu}} = 0.117 - 0.0591 \log[\text{Cl}^-] \quad (2)$$

Equation (1) yields an equilibrium potential of -0.25 V vs. SCE, and Equation (2) yields -0.10 V vs. SCE; both correlate well with the previous assignation of A_0 and A_1 peaks.

The increment in the anodic current observed at -0.1 V may be due to the activating effect of chloride ions. Copper dissolution proceeds according to Equations (3) and (4) [16]:



The anodic dissolution of copper is under the mixed control of the copper electrodisolution and the diffusion of soluble CuCl_2^- from the Helmholtz plane into the bulk solution. The local increment in the concentration of CuCl_2^- can result in the deposition of CuCl on the electrode surface, which protects the electrode and consequently decreases the current density [17]. This layer is porous [9,18], and the electrochemical reaction can continue through it. After the deposition of CuCl at the alloy surface, the deposit could be partially hydrolysed to give the more stable Cu_2O [18]. The CuCl formed in peak A_1 is obtained directly from Cu^0 and a small fraction from the Cu_2O formed in A_0 .

The equilibrium potential for the oxidation $\text{Cu}_2\text{O}/\text{CuO}$ is $+36$ mV vs. SCE [19]; then, peak A_2 may be related to the formation of CuO or $\text{Cu}(\text{OH})_2$. The formation of cupric-hydroxy chloride compounds on these materials is not expected [20].

As the potential scan reverses, the anodic peak A_3 is observed; it is more common for the BR (annealed) samples, together with two reduction peaks. The signal assigned to the A_3 peak could be related to a limited oxidation of copper to Cu^+ ions at the metal/ Cu_2O interface [21].

Comparing the voltammograms of the B (as cast) and BR (annealed) samples shown in Figure 5, both curves are similar in their morphology; nevertheless, a more in-depth analysis allows important distinguishing differences that could be explained in terms of the influence of their microstructures. As such, the curve corresponding to the B (as-cast) sample shows the highest current density for anodic peaks A_1 and A_2 . This highest current can be explained by the enhanced dissolution of this material result, probably from the dealuminisation reaction [22]. Peaks A_1 and A_2 are followed by a “passive” region of limiting current density. The relative value of this limiting current depends on the protective properties of the film formed anodically on the surface of the samples. The lower current registered for the BR (annealed) condition correlates with a more protective layer formed on its surface.

Moreover, the existence of a hysteresis loop on the return scan for B (as-cast) samples at the more positive potentials it is likely due to the loose protective properties of the surface corrosion layer [22]. The BR (annealed) samples do not present such a hysteresis loop, which seems to be related with the greater stability and better protective properties of the film formed on these samples.

After cyclic voltammetry, the morphology of the corrosion products covering the B (as cast) and BR (annealed) samples was analysed by SEM. Figure 8a,b shows the corroded surfaces for both materials. The surface of both samples was completely covered with corrosion products. Nevertheless, SEM images reveal a more compact structure for the film developed on the BR (annealed) samples, while the film developed on B (as cast) is more cracked (Figure 8a). The results are consistent with the less-protective character for B (as cast) detected from the cyclic voltammograms.

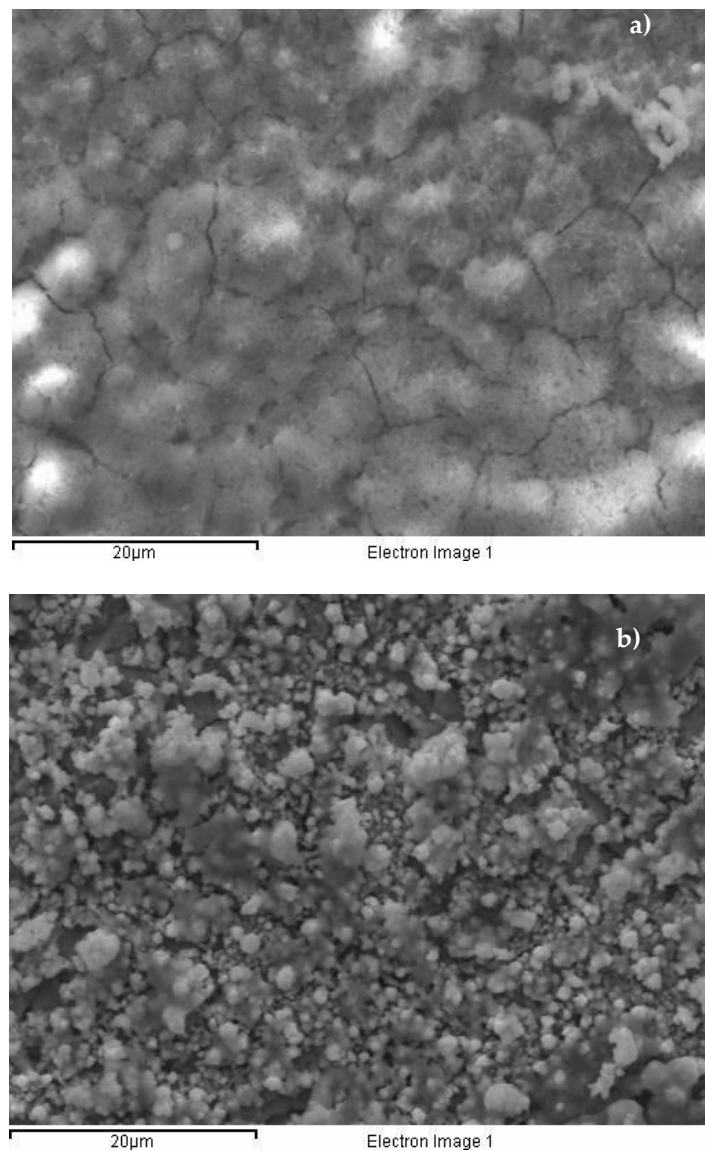


Figure 8. SEM images showing the surface morphologies for (a) a B (as-cast) sample and (b) a BR (annealed) sample after cyclic voltammetry in 3.5 wt.% NaCl solution.

3.5. Electrochemical Characterisation of the Corrosion Layers Formed at the OCP

The corrosion layers formed on the B (as-cast) and BR (annealed) samples, after 1 h of immersion time at their open circuit potential, OCP, were potentiodynamically reduced at a 1 mV s^{-1} scan rate. Figure 9 presents the obtained results. The measured OCP after 1 h of immersion was around -0.26 V vs. SCE for both samples, indicating that Cu (I) oxide was the main component of the surface products [17].

Figure 9 shows that the cathodic current values are lower for BR (annealed) samples than for B (as cast) samples. The current density measured for the B (as cast) samples was about 1.5 times higher than the corresponding current for the BR (annealed) samples. By analogy with Cu, the cathodic reaction of Cu-Al alloys in an aerated sodium chloride solution is well known to be the oxygen reduction, according to Equation (5):



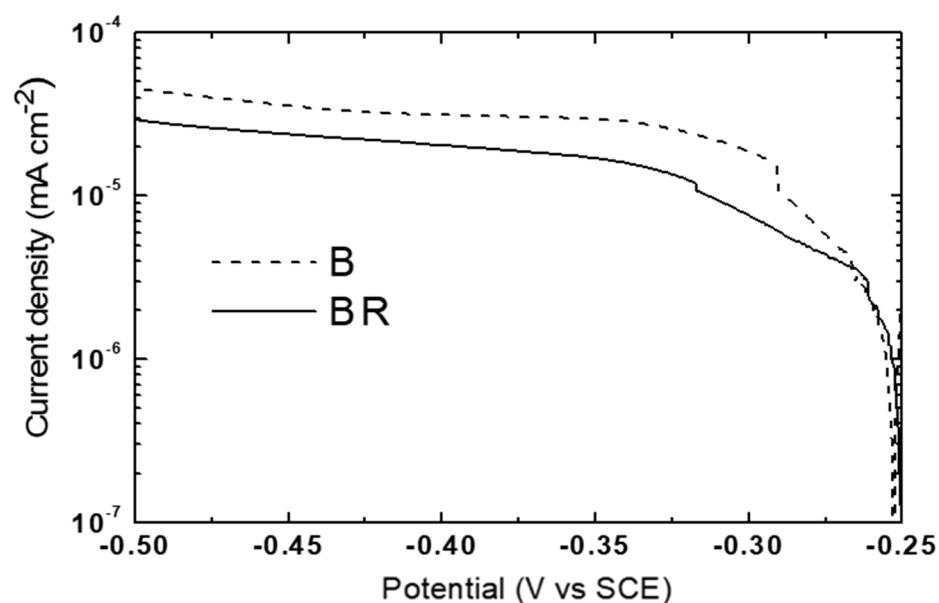


Figure 9. Polarisation curves obtained in 3.5 wt.% NaCl solution for B (as cast) and BR (annealed) samples from the OCP values to -0.5V at 1 mV s^{-1} .

It is known that for Cu based alloys, the oxide layer is protective because it restricts the cathodic oxygen reduction [2]. The role of Al, Ni and Fe in the passivation phenomenon of copper alloys was assumed to be due to its incorporation into the oxide lattice, reducing the rate of oxygen reduction at the oxide layer [23]. Thus, in agreement with the XPS data, the lowest current reduction for BR (annealed) samples may be explained in terms of the greater hindrance of O_2 reduction by a more important incorporation of alloying elements in the oxide layer of the BR material [24,25].

The cuprous oxide has only p-type semiconducting behaviour [26–29]; nevertheless, the incorporation of Al^{3+} and Ni^{2+} ions in the Cu_2O lattice increases the number of copper vacancies and decreases the number of electron holes of p-type Cu_2O oxide, which is manifested in an increase of electrical resistivity [21] and a consequent lowering of the oxygen reduction rate.

3.6. EIS Measurements

EIS measurements were performed in order to better understand the changes in corrosion properties and the evolution of the corrosion layer formed on B (as cast) and BR (annealed) samples as a function of the ageing time in chloride solution. The electrodes were dipped into the 3.5% NaCl solution, at pH 7.9, and then left at the OCP to reach a steady state.

In Figures 10 and 11, the Nyquist diagrams for the B (as cast) and BR (annealed) materials at several immersion times are depicted. The Nyquist diagrams recorded for both samples show a similar trend, displaying a qualitative change in size and shape at 72 h and 168 h of immersion for the B and BR conditions, respectively.

At times of less than 72 h, the Nyquist diagrams for the B (as cast) and BR (annealed) materials consisted in two parts: a high–medium frequency impedance arc, which is related to the charge transfer process, followed by a straight line at lower frequencies with a slope of 45° (a Warburg feature). The latter indicates that the corrosion process is limited either by the transport of oxygen from the bulk solution to the alloy surface, or by the transport of soluble corrosion products from the interface to the bulk solution. For times over 70 h for the B condition and 100 h for the BR (annealed) samples, the Warburg feature disappeared and the Nyquist diagrams seem to display a finite low-frequency limit.

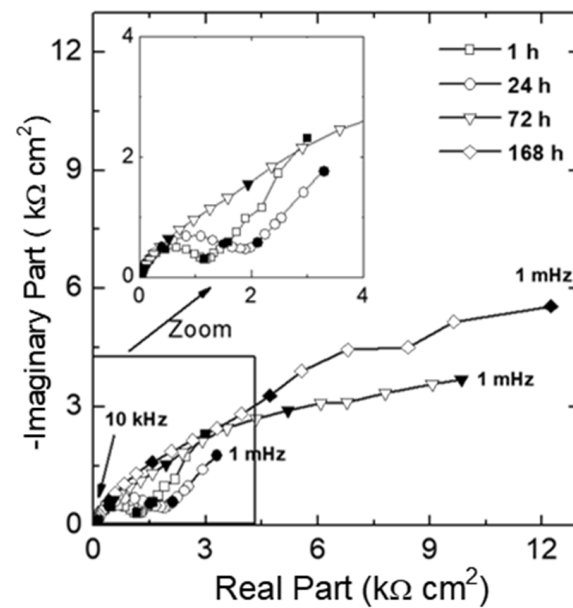


Figure 10. Nyquist diagrams of a B (as-cast) sample at different times of immersion in 3.5 wt.% NaCl solution.

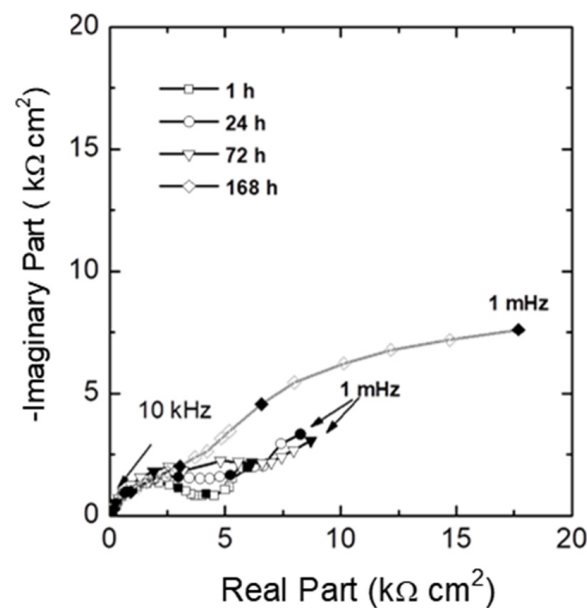


Figure 11. Nyquist diagrams for a BR (annealed) sample at different immersion times in 3.5 wt.% NaCl solution.

According to the literature [30], even at short immersion times, the electrochemical impedance response of copper can be ascribed to the formation of a porous film, initially mainly composed by Cu_2O , on the electrode surface, and the dissolution of copper with the formation of a CuCl layer [31] controlled by the transport of CuCl_2^- from the electrode to the bulk solution. If so, the diffusion effect should be attributed to the transport of CuCl_2^- .

The changes in the impedance spectrum in size and shape detected after 70 h indicate variations in the corrosion process which are likely related with changes in the oxide layer structure. The Bode diagrams depicted in Figure 12 show the reported changes for both materials at short and long immersion times in the chloride solution.

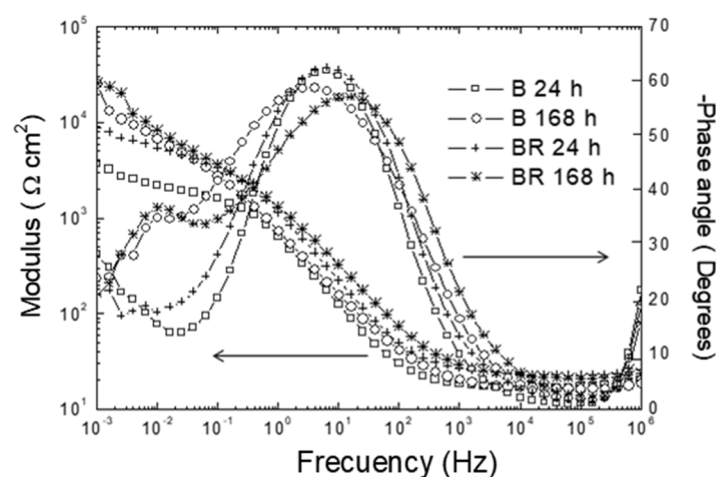


Figure 12. Bode diagrams for B (as-cast) and BR (annealed) samples after different times of exposure to 3.5 wt.% NaCl solution.

During the analysed time period, the OCP shifted towards more anodic values from -0.25 V SCE to -0.15 V SCE. Figure 13 displays the evolution of the OCP with time. According to the corrosion mechanism of these alloys, a progressive covering of the electrode surface by a precipitated CuCl layer allows an explanation of the evolution of the OCP. Furthermore, the progressive anodic shift of the OCP takes place in parallel to the disappearance of the Warburg feature in the impedance spectra. Then, it could be postulated that as the potential becomes more anodic, a layer of CuCl builds up, leading to a blocking effect and the appearance of a second capacitive loop, which can be assigned to a diffusion process of the anodic species within the CuCl salt layer. Instead of a semi-infinite diffusion (Warburg feature), a finite length diffusion is now considered [32]. Furthermore, the OCP values measured for the “as-cast” material evolve more rapidly, which may indicate faster oxidability for B samples with respect to the annealed samples.

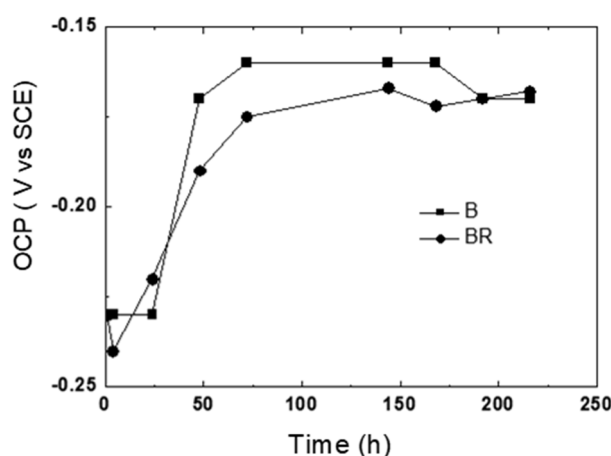


Figure 13. Variation of the OCP values with the immersion time in a chlorinated solution.

Because of the observed changes in the EIS response, for the fitting of the experimental data, two different equivalent circuits were required, which include either a Warburg element, Z_w , or bounded diffusion impedance, Z_d , as depicted in Figure 14. For short immersion times, the experimental data could be reasonably fitted using the Warburg element, while for longer immersion times, Z_d was employed.

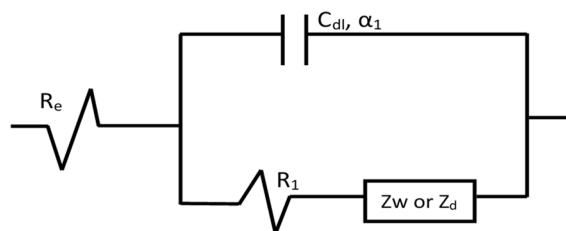


Figure 14. Electrical equivalent circuit used for the fitting of EIS experimental data. Z_w was employed in the first 70 h for the B samples and the first 100 h for the BR samples. Z_d was employed for longer immersion times.

In Figure 14, R_e represents the electrolyte resistance, R_1 corresponds to the charge transfer resistance, and C_{dl} corresponds to the double-layer capacitance. α_1 is a Cole-Cole dispersion parameter of the $R_1 C_{dl}$ time constant. The impedance, $Z(\omega)$, of that circuit is given in Equation (6), where $j = \sqrt{-1}$ and $\omega = 2\pi f$.

$$Z(\omega) = \frac{R_1}{(j\omega R_1 C_{dl})^{\alpha_1} + \frac{R_1}{R_1 + (Z_d \text{ or } Z_w)}} \quad (6)$$

The Warburg, Z_w , and diffusion bounded impedance, Z_d , are defined in Equation (7) [33,34].

$$Z_w = \frac{\sigma}{\sqrt{\omega}}(1 - j) \\ Z_d = R_d \frac{\tanh(\sqrt{(j\omega\tau_d)^{\alpha_d}})}{\sqrt{(j\omega\tau_d)^{\alpha_d}}} \quad (7)$$

In Equation (7), the parameters α , R_d and τ_d contain information about the diffusion coefficient of the diffusing species. τ_d is the time constant of the diffusion process. A Cole-Cole type dispersion parameter, α_d , was also included for this time constant.

In the fitting procedure, the experimental data were truncated at 10^5 Hz to avoid the capacitive contribution of the reference electrode, which is evident in Figure 12 at the high-frequency limit.

The good agreement between the experimental and fitted data to the proposed equivalent circuits is shown in the Nyquist diagrams depicted in Figure 15, corresponding to a B (as-cast) sample at 24 h and at 192 h of immersion.

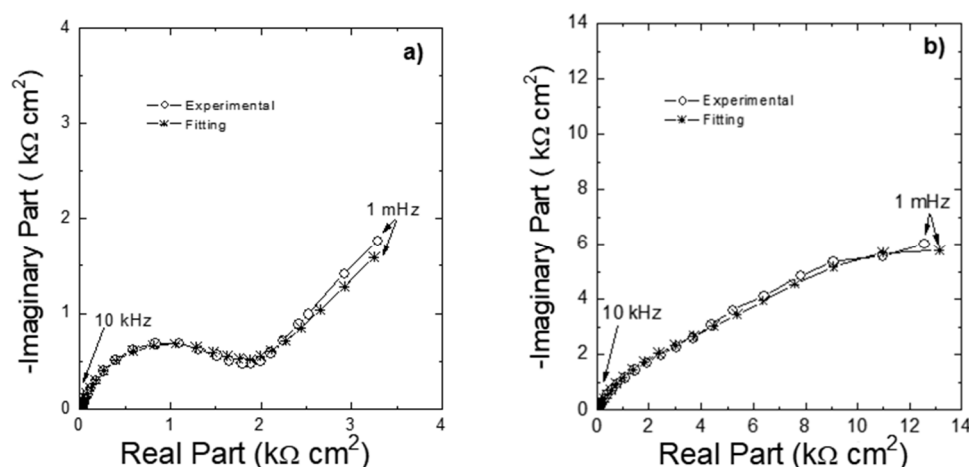


Figure 15. Measured ($\circ$) and fitted ($*$) Nyquist plots for a B (as-cast) sample (a) at 24 h of immersion and (b) at 192 h of immersion (b).

The values of the calculated best-fitting parameters for both materials using the proposed equivalent circuits are displayed in Tables 5 and 6.

Table 5. Values of the fitting parameters for a B (as-cast) sample at different immersion times in the chlorinated solution.

Time (h)	R_e ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	C_{dl} (μFcm^{-2})	α_1	W ($\Omega \text{ cm}^2 \text{ s}^{-1/2}$)	R_d ($\Omega \text{ cm}^2$)	τ_d (s)	α_d
1	17	1111	183	0.82	128	-	-	-
4	17	2028	280	0.82	124	-	-	-
24	17	1729	253	0.80	124	-	-	-
48	17	2465	193	0.77	299	-	-	-
72	17	1959	194	0.75	-	10,550	42.0	0.80
144	17	4381	378	0.70	-	15,684	116.4	0.84
168	16	5108	442	0.70	-	12,553	76.4	0.95
192	17	6400	631	0.67	-	15,038	128	0.68

Table 6. Values of the fitting parameters for a BR (annealed) sample at different immersion times in the chlorinated solution.

Time (h)	R_e ($\Omega \text{ cm}^2$)	R_1 ($\Omega \text{ cm}^2$)	C_1 (μFcm^{-2})	α_1	W ($\Omega \text{ cm}^2 \text{ s}^{-1/2}$)	R_d ($\Omega \text{ cm}^2$)	τ_d (s)	α_d
1	22	3826	138	0.77	154	-	-	-
4	22	4083	154	0.77	152	-	-	-
24	22	4510	186	0.76	290	-	-	-
48	23	6591	215	0.76	268	-	-	-
72	23	6469	247	0.73	267	-	-	-
144	22	4187	113	0.72	-	15,792	30.2	1
168	21	3462	126	0.71	-	18,769	62.3	1
192	21	3648	130	0.61	-	17,321	68.0	1

A first look to Tables 5 and 6 reveals that the R_e values for the BR (annealed) material are higher than those obtained for the B (as-cast) material. As the electrolyte and cell geometry are invariant, that difference in R_e can only be attributed to a dissimilar surface resistivity, which can be explained through the incorporation of Ni and Al ions into the crystal lattice of the Cu oxides. This incorporation increases the number of copper vacancies and decreases the number of electron holes of the p-type Cu_2O oxide, which increases the electrical resistivity of the oxide [21]. Thus, the higher R_e for the BR (annealed) sample correlates well with previous data and may be explained in terms of a greater incorporation of Al and Ni ions into the oxide formed on its surface.

At short immersion times, both the C_{dl} and R_1 values rise, which is in agreement with the OCP evolution. The OCP values may be explained in terms of the accumulation of precipitated corrosion products on the electrode surface. These products increase the roughness of the electroactive surface, which leads to higher C_{dl} values. For the B samples, the C_{dl} values are higher than for the BR (annealed) samples, by almost twice, which could be ascribed to the formation of a more defective and porous surface layer. The progressive accumulation of corrosion products also acts by blocking the porous surface, and R_1 increases. The lower R_1 values for the B (as-cast) samples in comparison with the annealed material evidences a faster charge transfer process across the double layer. Moreover, for each of the analysed immersion times, the values of the Warburg coefficients were slightly higher for the BR (annealed) samples. Both the higher R_1 and the larger Warburg coefficients for BR might indicate a higher corrosion resistance for this material.

At immersion times over 70 h for the B (as-cast) material and 100 h for the BR (annealed) material, the accumulation of corrosion products on the electrode surface starts to become important, and the blocking effect begins to dominate the corrosion process. Now, the impedance spectra were best fitted to a model of linear diffusion through a finite layer.

For the annealed sample, C_{dl} and R_1 remain practically constant at times over 100 h. This could indicate that some kind of steady state was achieved. However, for the B (as

cast) samples, the C_{dl} and R_1 values still maintain a trend to increase even at the longest immersion times, which could indicate that the oxide layer formed on this sample is not yet stabilised. At that stage, R_d mostly dominates over R_1 ; as such, it defines the corrosion rate.

4. Conclusions

The influence of annealing on the microstructure and corrosion resistance of a complex copper aluminium alloy was studied in this paper, and the following conclusions can be drawn:

1. The microstructure of the B (as-cast) samples consists of α grains, some retained β -phase, and precipitates of the K-phase. Annealing induces a refinement of the α -phase grain size; the retained β -phase disappears and increases the density of fine K-phase precipitates in the α -phase.
2. Microstructural changes play an important role in dealloying corrosion resistance and in the properties and structure of the oxide layer grown. As such, the dealloying corrosion resistance of annealed samples is better than that of “as-cast” samples. The better resistance for the BR (annealing) sample is justified in terms of more homogeneous microstructure, which does not allow the existence of a continuous path for dealuminisation, and also limits the presence of sites available for galvanic coupling.
3. In chloride-containing media, the oxide layer developed on “as cast” and annealed samples in OCP conditions is formed basically for Cu_2O . Nevertheless, differences in the composition of the air-formed layer and in the electrochemical reduction curves evidence changes in the properties and composition of these cuprous oxides. The obtained results indicate, as a consequence of the more homogenised microstructure, a larger incorporation of Cu^{2+} , Ni^{2+} , and Al^{3+} into the structure of the Cu (I) oxide formed on the BR (annealed) samples.

The greater incorporation of Cu^{2+} , Ni^{2+} , and Al^{3+} in the oxide layer improves the corrosion resistance. This improvement is indicated by the lower current density registered for the BR (annealed) samples in the cyclic voltammograms at all of the scanned potentials, and by the EIS spectra, which indicate that the B (as-cast) samples are easily oxidized, finally resulting in poorer corrosion resistance.

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