

Bronze degradation processes in simulating archaeological soil media

Hèla Hassairi · Latifa Bousselmi · Ezzeddine Triki

Received: 2 March 2009 / Revised: 26 May 2009 / Accepted: 2 June 2009 / Published online: 30 June 2009
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Abstract The purpose of this study is to establish reliable procedure reproducing the degradation processes that occurred on the archaeological artefacts before their excavation. Two simulating soil media are chosen, the first one (FJ) is made from archaeological soil filtrate and the second is a chloride- and/or sulphate-containing solution (CSJ) taken at the same soil amounts of aggressive ions. According to stationary studies, corrosion mechanism in CSJ medium is catalysed by the presence of chloride at the surface of tin bronze electrode, but sulphate products tend to stabilise the surface of bronze sample immersed in soil filtrate. In FJ, the trend of impedance spectra remains unchanged during the immersion period. Adjusted impedance parameters prove that passivation and depassivation can occur simultaneously on bronze surface with different expansion. In CSJ, impedance data evolve according to the immersion time. The evolution of adjusted parameters according to the immersion time describes well the surface state of the bronze sample. The corrosion process is more difficult while the metallic surface is covered with a bronze corrosion layer “patina” which explain the capacitance decreasing and the resistance increasing (after 50 days). Scanning electron microscopy observations coupled with energy-dispersive X-ray spectrometry analysis approve our electrochemical results.

Keywords Bronze · Corrosion · Electrochemical studies · Simulate soil medium

Introduction

Nowadays, the study of new alloys and the validation of their corrosion resistance through tests carried out in several aggressive environments provide interesting information for the applications in the field of cultural heritage [1]. Nevertheless, after the excavation, the sudden change of the environment breaks off the equilibrium obtained over a long period and sometimes induces an acceleration of the corrosion processes. This may lead to a complete decomposition of the archaeological object within a very short period [2]. Consequently, preservation of our archaeological heritage requires a good knowledge of the causes of soil corrosivity. Soil research and metallurgical analysis are necessary to review the conditions at archaeological sites and to develop suitable protection methods [3, 4].

Studies of the degradation of metal artefacts related to soil type revealed that the most important soil parameters are considered to be soil texture, soil acidity, and the amount of soluble salts, such as chlorides and sulphates, which promote the corrosion of metal objects [3, 5-8].

Bronze corrosion has been the subject of several papers [9-18] that report its major products as oxides and basic salts of copper. A decuprification process model has been proposed by Robbiola et al. [9, 10]. Two types of corrosion structures have been identified: type I structure has been defined as an Sn-enriched passivating layer, which preserves the original surface of the artefact. A rough three-layered patina characterises type II structure, corresponding to a more severe attack, with an outer layer enriched in copper compounds.

H. Hassairi (✉) · E. Triki
Unité de Recherche Corrosion et Protection des Métalliques,
ENIT,
1002 Tunis, Tunisia
e-mail: helahassairi@yahoo.fr

H. Hassairi · L. Bousselmi
Laboratoire de Traitement et Recyclage des Eaux Usées,
Centre des Recherches et des Technologies des Eaux,
Technopole Borj Cedria,
8020 Soliman, Tunisia

Many studies were carried out on synthetic bronze alloy in different aggressive media simulating the burial context either by using chloride- or sulphate-containing solution.

Studies in chloride media have been undertaken by many authors [11–15]. It has been demonstrated that the passive layer on copper is composed by copper oxides and copper chlorides, although complex ions may also be formed, i.e., CuCl_2^- and CuCl_3^- , depending on the pH and chloride concentration. More recent study [16] concludes that the mechanism of bronze oxidation, in NaCl 0.1 M, involves at least two parallel processes: alloy oxidation at the alloy/layer interface and copper dissolution at the layer/electrolyte interface, tin species remaining in the corrosion layer.

Mabille et al. [17] affirm that the use of a 0.01 M Na_2SO_4 solution allowed us to simulate corrosion conditions in low aggressive conditions. The global nature of the studied corrosion layers, confirmed later by Sidot et al. [18], matches the type I model of blocking adherent layers (bronze patina) observed on ancient bronzes. Their formation is the result of a decuprification mechanism with occurs through the following steps: tin, the less noble component of the alloy, oxidises first, leading to a passivating tin oxide layer.

Few works [19, 20] have been interested to the behaviour of copper in chloride and sulphate-containing solutions. They have observed pit morphology depending on the relative concentration of both anions and concluded that the aggressiveness of one species towards the corrosion of copper can be modified by the presence of other species. However, as remarked by those authors, the synergetic effect of various anions remains unclear and deserves further studies to understand the electrochemical behaviour of copper alloy in soil or in further simulating media.

On this basis, two simulating archaeological soil media have been chosen to evaluate the electrochemical behaviour of a tin bronze alloy. The first one (FJ) is made from archaeological soil filtrate, and the second is a chloride and sulphate-containing solution as explained below. A stationary study enables us to perceive the combined effect between the two aggressive ions, chloride and sulphate. Electrochemical impedance technique was performed to characterise the bronze/electrolyte interface. We will also report the investigation performed on patina formed on the bronze surface by scanning electron microscopy (SEM) observations coupled to energy-dispersive X-ray spectrometry (EDS) analysis.

Experimental conditions

The bronze alloy This study concerns the corrosion behaviour of a Cu-based alloy, Cu-9.4Sn, whose composition is similar to ancient alloys excavated in Tunisia and related to Punic period [13]. The material is produced by

Consiglio Nazionale delle Ricerche-Istituto per lo Studio dei Materiali Nanostrutturati in the frame of EFESTUS Project funded by the European Commission.

Characteristics of corrosive media The first simulating archaeological soil medium (FJ; J stand relative to Jama soil) was constituted by the filtration of the solution obtained from a mixture of distilled water and Jama soil at the ratio 5:1 steered during 24 h. The chemical composition of this soil was presented in a previous work [21].

The second aggressive medium used in this study (CSJ) is a solution containing both aggressive ions Cl^- and SO_4^{2-} at the same amounts being in Jama soil [21] (0.3 and 9.8 mg g^{-1} equivalent to 0.02 and 0.125 M, respectively, for chloride and sulphate ions, while taking into account the value of soil density: 1.23 g cm^{-3}). The pH value of this medium was adjusted at 8.5 to be equal to FJ medium and soil pH using a solution of sodium hydroxide (0.1 M).

CJ and sulphate (SJ) media are used during the stationary study to elucidate the electrochemical effect of each aggressive ion. CJ is composed by a NaCl solution (0.02 M), and SJ is a sodium sulphate solution (0.125 M). The pH value of both media is adjusted at 8.5.

Electrochemical cell The cell was a conventional three electrodes; a saturated calomel electrode was used as reference and platinum as counter electrode. The working electrodes were made of bronze alloy polished mechanically using successive grades of SiC paper up to 2,500.

Experiments were carried out on a PGP 201 TACUSSEL potentiostat. All the potentiodynamic measurements were performed at a scanning rate of 25 mV min^{-1} . Electrochemical impedance spectroscopy (EIS) investigations are carried on Solartron 1286 potentiostat equipped with a 1250 frequency-response analyser. The frequency range is from 65 KHz to 10 mHz with five points by decade.

Analysis SEM-EDS were employed to investigate corrosion layer structure and to identify the atomic percentage both by imaging and by line spectra. Results were obtained by a Quanta 200 low-vacuum scanning electron microscope with a tungsten electron source, with three imaging modes to accommodate the widest range of samples of any SEM system.

Results

Stationary study

Steady state electrochemical study was realised using the bronze electrode in the simulating Jama soil media FJ and CSJ. This survey involves two parts. The first one is

consecrated to the follow-up of the potential values according to the immersion time, while the second one clarifies the cyclic voltammetric behaviour of the bronze in different selected media.

Stationary studies describe also the bronze behaviour in FJ and CSJ media in comparison with separately chloride and sulphate-containing solutions (respectively CJ and SJ), in order to elucidate the aggressiveness of each medium and to clarify the corrosion mechanisms relative to each aggressive ion.

$E_{o,c}$ evolution recorded for the bronze alloy in the four selected media during various immersion times is gathered in Fig. 1.

Free potential curves show similar evolution according to the immersion time characterised by an ennoblement of $E_{o,c}$ values after 30 min of immersion followed by a stabilisation.

A difference of 30 mV is recorded between the two simulate media (FJ and CSJ) at the beginning of the immersion. This difference increases according to the immersion time and reaches 50 mV after 1 h of immersion. However, potential values obtained in FJ and sulphate-containing solutions are very close during the immersion time; the difference is about 8 mV.

At the first time of immersion, the free potential value relative to the bronze alloy in CSJ medium (-127 mV) was positioned between values obtained in CJ and SJ medium (respectively, -168 and -87 mV). However, $E_{o,c}$ value obtained in CSJ medium rejoin the value registered in CJ after 60 min of immersion.

Corrosion products formed at the surface of bronze electrode in the sulphated medium (SJ) were more protectors than those formed in presence of chloride ions. The presence of the two aggressive ions (CSJ medium) awarded to the interface behaviour between these two extreme at the beginning of the immersion, but which have the tendency to confound to values obtained in CJ medium after 60 min. The soil filtrate medium appears less aggressive than the second simulating medium.

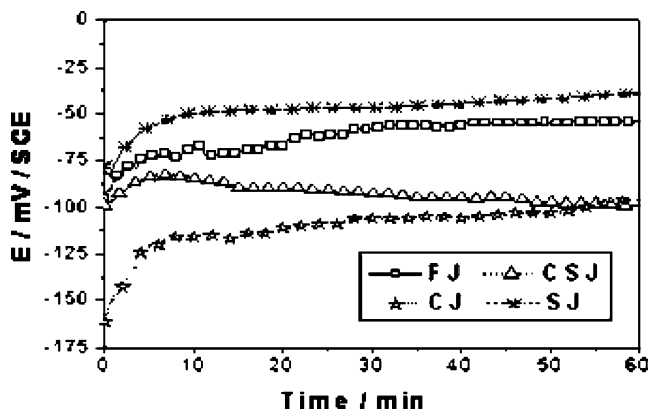


Fig. 1 Evolution of open circuit potential values ($E_{o,c}$ /mV) according to the immersion time in selected media

After 1 h of immersion, typical voltammograms for the bronze alloy, swept from $E_{o,c}$ to $+1,500$ then to $-1,500$ mV, are plotted and shown in Fig. 2. Voltammograms trends obtained in selected media (Fig. 2) permit us to postulate that the electrochemical behaviour of the bronze alloy in FJ medium is assigned to the effect of chloride, while the one observed for CSJ medium is attributed to the effect of sulphate ions.

In FJ medium, cyclic voltammetry shows a passive layer breakdown at about 98.5 mV followed by an increase of current values overall the potential range (until 5.06 mA cm^{-2}). This trend can be attributed to the simultaneous dissolution of alloy species. A same behaviour was detected at $E < 500$ mV in Jama soil medium [21]; but beyond this potential value, a different shape was observed, characterised by an increase of current density values relative to the oxidation of both copper and tin species.

In chloride-containing solution, polarisation curves show also two overlapped anodic peaks related to the presence of chloride ions.

These peak potentials are included in the potential interval of the first peak detected in CSJ medium, from where we can deduce that in chloride medium, there is a separation of the dissolution of each metallic species.

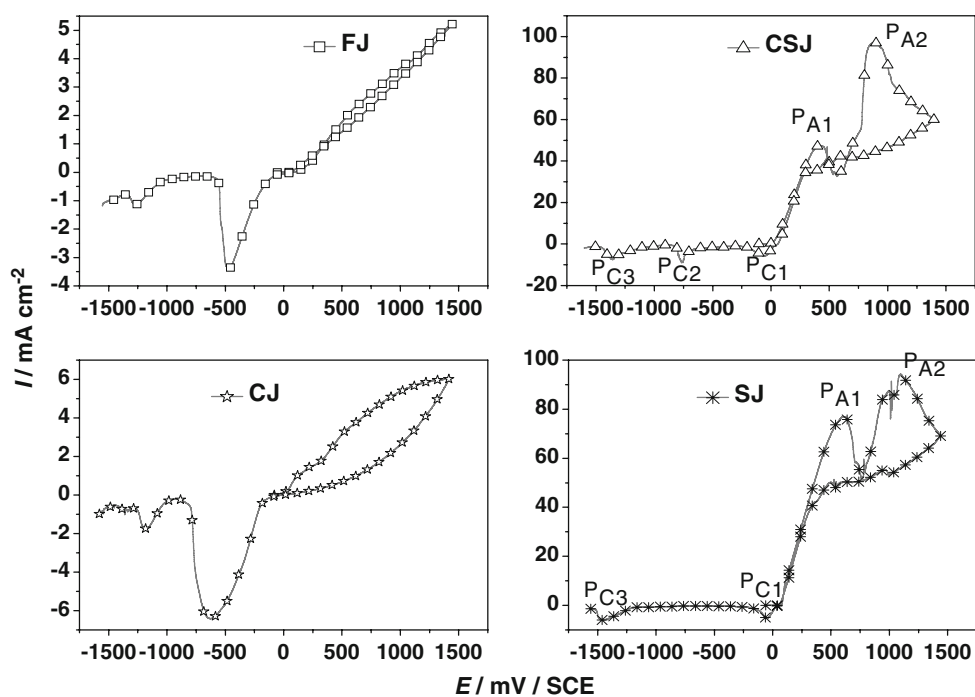
The reversed scan in FJ and CJ media show that the anodic current dropped indicating an irreversible process. In addition, two cathodic peaks were detected. The first one, which appears at -474.75 mV, is to be linked to the reduction of the copper layer compounds: cuprous oxide to copper and cupric species to cupric ion [22–24]. The second peak reached at $-1,009.4$ mV, with a current density of -1.08 mA cm^{-2} , is attributed to the reduction of Cu_2O to copper and SnO_2 to tin [12].

These peaks are also observed in our previous study realised in Jama soil medium but at lower intensities. This phenomenon was partially due to the increase in thickness resulting from charge quantity involved during the reduction process [12].

In CSJ, anodic polarisation curves started with a passive domain at the potential intervals ($E_{o,c}$, 20 ± 3 mV). This passive region was followed by two anodic peaks designated by P_{A1} (416.9 mV) and P_{A2} (875.8 mV). These two peaks appear also at the same potential values in SJ medium, so they are caused by the presence of sulphate ions. The first one is attribute to the dissolution of copper and tin species and transformation/formation of corrosion compounds [13, 17, 25, 26]. The second anodic peak is relative to the formation of copper and tin sulphate species [18, 27, 28].

Results obtained in CSJ medium are in agreement with those obtained in a previous work of E. Sidot et al. [18], who deduce that higher concentration of sulphate anions in the electrolyte, on one hand, increases the dissolution of copper and tin and the formation of (hydroxyl) oxide

Fig. 2 Cyclic voltammograms recorded in selected media (scan rate 25 mV min^{-1})



compounds but, on the other hand, may favour the formation of stable and blocking tin sulphate compounds on the surface layer bronze electrodes.

The follow-up of the reverse scan in CSJ let appear three cathodic peaks designated by P_{C1} , P_{C2} , and P_{C3} , respectively, at -65.7 , -750.1 , and $-1,341.7$ mV. According to the bibliography, these cathodic peaks are attributed respectively to the reduction of cuprous oxide to copper and of cupric species to cupric ion [22, 23, 29, 30], to the reduction of tin species [13, 18], and to the reduction of copper-sulphated species [18, 24, 30]. In sulphate-containing solution, only the first and the third peaks are present.

According to the work of Duthil et al. [19] and Mankowski et al. [20], who studied the synergetic effect of chloride and sulphate ions on the pit morphology on copper surface, the CSJ medium corresponds to region II. In this region, defined by $[Cl^-] > 5 \cdot 10^{-4}$ and $[Cl^-]/[SO_4^{2-}] < 5$, the electrochemical behaviour let appear characteristics of both aggressive ions: sulphate and chloride. Corrosion layers are characteristic of sulphate-containing solutions, but a $CuCl$ layer characteristic of chloride solutions can also be formed on the copper alloy surface.

EIS investigation

The EIS tests were performed to evaluate the change of characteristic parameters for corrosion behaviour with increasing immersion time. The impedance diagrams were obtained in the Nyquist representation at $E_{o,c}$ between 65 KHz and 10 mHz in CSJ and FJ media.

Figure 3 shows some impedance diagrams recorded under open circuit conditions during the time, relative to the bronze alloy immersed in FJ medium.

EIS diagrams were characterised by one capacitive loop followed by a diffusion process relative to low frequency domain (slope of 45°). The high frequency loop is generally considered as due to a charge transfer process. The loop in the lower frequency range has been shown to correspond to a mass transport contribution due to the process of metal dissolution [12].

This behaviour was the same from 1 h of immersion until 70 days of immersion. The interface behaviour is considered equivalent to the electrical circuit of Fig. 4. The proposed equivalent circuit seems to fit the physical process and the data quite well.

This trend of diagrams was also observed in Jama soil medium after 20 days of immersion for the same bronze alloy and after only 1 day for a leaded tin bronze [21].

Figure 5 shows some impedance diagrams recorded under open circuit conditions during the time, relative to the bronze alloy immersed in CSJ medium.

The impedance data obtained after 1 h of immersion in CSJ show an apparent single capacitive loop relative to high frequency region followed by a diffusion process characterised by 45° slope corresponding to a mass transport contribution due to the metal dissolution [1, 12]. This trend was the same observed for sample immersed in FJ. In a previous study [31] realised in chloride medium, using Cu electrode, the same trend of diagrams was observed. The semi circle at high frequency was attributed

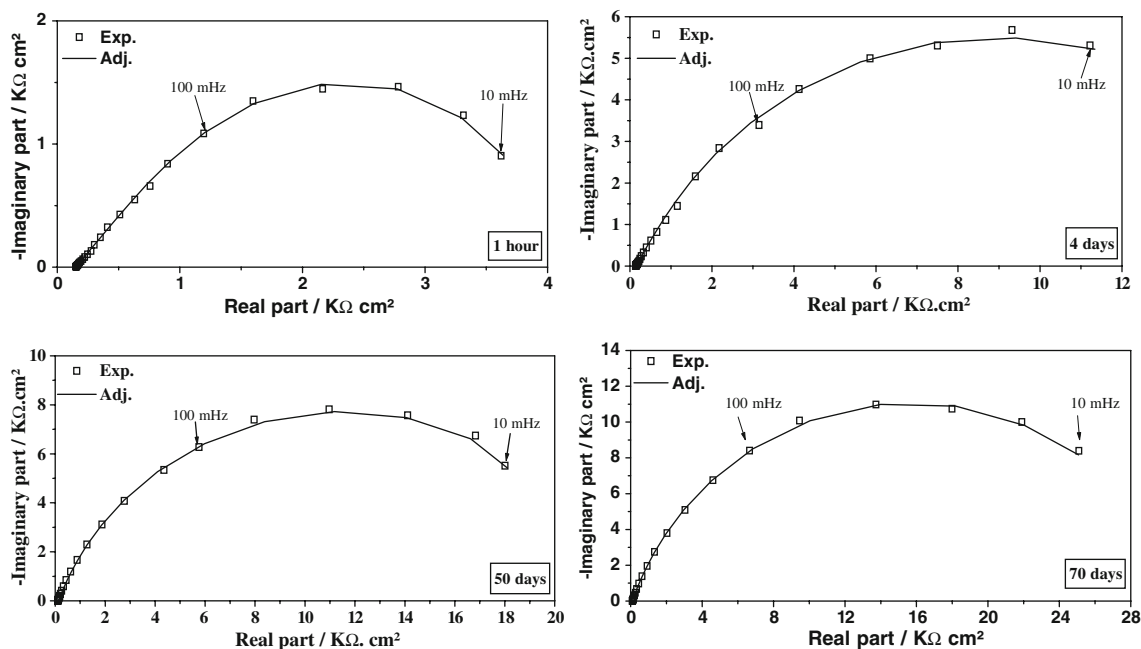


Fig. 3 Nyquist plots recorded in FJ medium after 1 h, 4, 50, and 70 days of immersion

to the modulation of CuCl adsorbed at the electrode; whereas, the low frequency part of the diagram represents the diffusion process at the electrode due to CuCl_2^- .

From 2 days of immersion, a second capacitive loop appears, at high frequency domain, which could be due to a mixed activation-diffusion control of the dissolution reaction of copper [12]. When the immersion time increased (from 50 days), a third single loop appeared, and it is related to the accumulation of corrosion product layer on the surface of the bronze sample [18].

A best fitting is obtained using the equivalent circuit shown in Fig. 6. The impedance Z of decentralised R//C loop is represented by the following expression (Eq. 1):

$$Z = \frac{R}{1 + (2 \int \int RC)^{\alpha}}, \tag{1}$$

which takes into account the deviation from the ideal RC behaviour ($0 \leq \alpha \leq 1$) in terms of time constants distribution linked to surface inhomogeneities, roughness, and variation in layer properties [32].

The electrolyte resistance (R_s) registered in FJ and CSJ media decreases according to the time of immersion and reach, respectively, 94 and $2.3 \Omega \text{ cm}^2$ after 70 days of

immersion. The decreases could be linked to the enrichment of the electrolyte with metallic ions on the interface.

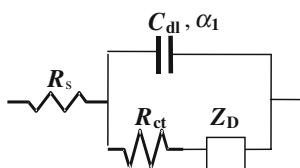
The evolution of R_{sf1} C_{sf1} time constant for the sample immersed in CSJ medium, according to the immersion time, is depicted in Fig. 7. The R_{sf1} parameter tends to increase with exposure time. This raise can be due to the accumulation of corrosion products at the surface of the sample. Parallel to that evolution, the surface layer capacitance, C_{sf1} , is decreasing until 50 days, reflecting the growth of the film of corrosion product. Since this exposure time (50 days), the capacitance values keep more or less constant; as a consequence, a second time constant relative to HF region appears.

The evolution of C_{sf2} and R_{sf2} parameters is quite similar to those relative to the first HF loop.

The evolution of R_{ct} C_{dl} time constant for samples immersed in FJ medium is depicted in Fig. 8a. Some fluctuations in the capacitance and resistance values are observed during the first 6 days of immersion. Then R_{ct} parameter tends to decrease and reaches a minimum at 18 days of immersion. Parallel to that evolution, the double layer capacitance, C_{dl} , is increasing. The interval between 18 and 70 days is characterised by an increase in resistance and decrease in capacitance with exposure time; at the end of this interval, these parameters keep more or less constant.

The fluctuations in the capacitance and resistance values reflect the variability of the active surface where corrosion process occurs and, hence, the effectiveness of passivation. In that sense, it is remarkable that in the dynamic nature of

Fig. 4 Equivalent circuit model, R_s : solution resistance, R_{ct} : charge transfer resistance, C_{dl} : double layer capacitance, and Z_D (R_D, τ_D): diffusion impedance



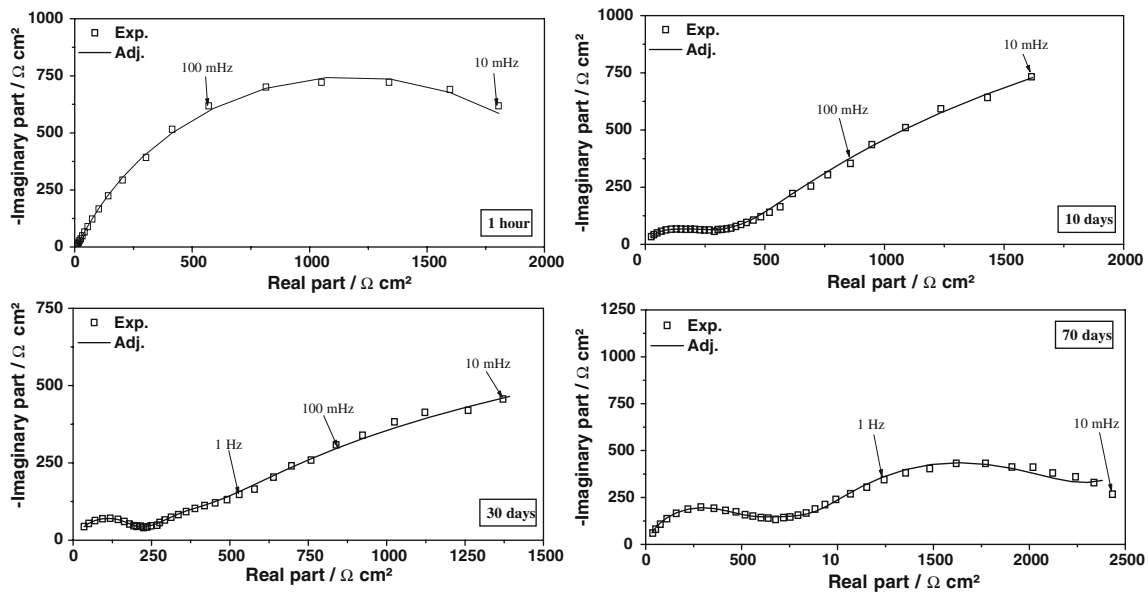


Fig. 5 Nyquist plots recorded in CSJ medium after 1 h, 10, 30, and 70 days of immersion

this phenomenon, passivation and depassivation can occur simultaneously on bronze surface with different expansion.

Figure 8b depicted the R_{ct} and C_{dl} evolution according to the exposure time in CSJ medium. These parameters fluctuate inversely during 30 days of immersion. After that, R_{ct} and C_{dl} undergo an important increase, which is related to corrosion products: as the amount of them is larger, the double layer capacitance rises and, due to those compounds, offer a good barrier against aggressive electrolyte; the charge transfer resistance is increasing as well. Since 50 days of immersion, the corrosion process become more difficult, while the metallic surface is covered with a bronze corrosion layer “patina” which explain the capacitance decreasing and the resistance increasing.

The diffusion resistance values registered in CSJ medium are weaker than those obtained in FJ medium.

A quick increase of R_D value was detected as soon as the immersion, then a pseudo plateau appears from 8 days of immersion. In FJ medium, R_D values enhance again and

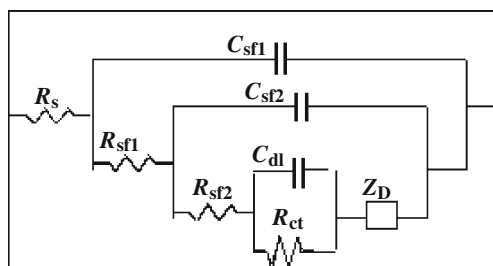


Fig. 6 Equivalent circuit model, R_s : solution resistance, R_{sf1} : first surface layer resistance, C_{sf1} : first surface layer capacitance, R_{sf2} : second surface layer resistance, C_{sf2} : second surface layer capacitance, R_{ct} : charge transfer resistance, C_{dl} : double layer capacitance, and Z_D (R_D , τ_D): diffusion impedance

attain $31 \text{ K}\Omega \text{ cm}^2$ after 70 days of immersion, but they remain more or less constant in CSJ medium, indicative that the surface state is passivating (Fig. 9).

As can be seen from the evolution of adjusted parameters relative to CSJ medium, the corrosion layer evolves according to the time reinforces and then stabilises. This phenomenon is to be joined to the effect of the corrosion products/soil interface that could play an important role in the evacuation of the copper ions produced by the process of decuprification [21].

Characterization of corrosion layers by SEM-EDS analysis

It is necessary to link this electrochemical behaviour to the structure and composition of the corrosion product layer to

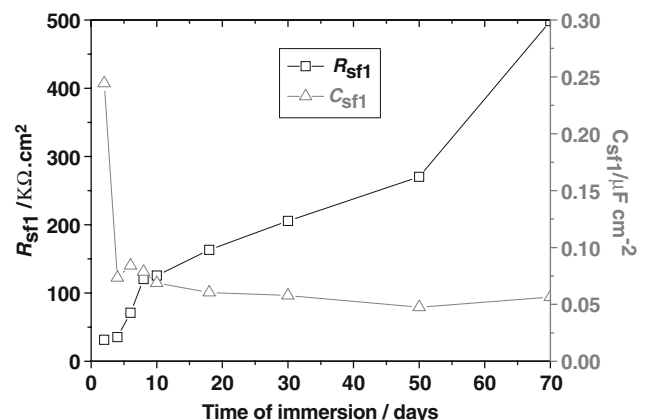


Fig. 7 Evolution of R_{sf1} and C_{sf1} parameters according to the time of immersion in CSJ medium

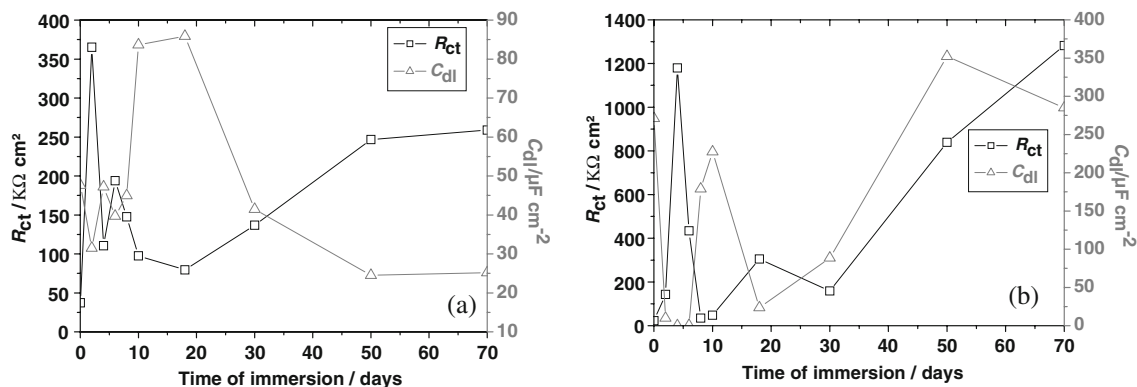


Fig. 8 Evolution of R_{ct} and C_{dl} parameters according to the immersion time in FJ (a) and CSJ (b) media

define the degradation process. SEM-EDS analysis is performed on bronze sample after 20 days of immersion in FJ (Fig. 10) and CSJ (Fig. 11) media.

A more or less compact and uniform corrosion layer was observed on bronze sample immersed in FJ medium. The surface let appear some crevices. As can be seen from EDS microanalysis, the corrosive layer ((a) and (b)) contains copper and tin with large amount of oxygen which explain the presence of Cu and Sn oxides. Crevices were analysed by EDS (c) and reveal the presence of chloride, sulphate with higher content of copper, and tin, which characterise the internal tin-enriched layer, often linked to the presence of oxide or hydroxide compounds, with a relative enrichment in Cl content. Soil elements such as Fe, Si, Ca, and P are also detected in the corrosion layer.

Different surface states with thick corrosive layer, fissures, and cracks were observed for sample immersed in CSJ corrodent (a). This corrosive features is due to a mechanical breakdown resulting from internal stresses relative to the decuprification process. The elementary content reveals the well-defined contribution of aggressive ions (sulphate and chloride) ((b) and (c)) in association to high amount of copper and tin. Much higher copper content in corrosion layer indicated that the copper particle was diffused into the corrosion layer due to the tendency of Cu dissolution into the corrosion layer.

Conclusion

The steady state behaviour of tin bronze in simulating archaeological soil media is related to the presence of aggressive ions, chloride, and sulphate. The ennoblement of corrosion potential, obtained after 1 h of immersion, is to be linked to the formation of a corrosion layer at the surface of bronze electrode. This layer was characterised by the presence of protector sulphate compound in FJ but contains more chloride compound in CSJ.

Chlorides act as a catalyst for corrosion mechanism in CSJ medium, but sulphate products tend to stabilise the surface of bronze sample immersed in soil filtrate.

The EIS investigation characterises the interface behaviour in both selected media. In FJ, the trend of diagrams remains the same. The charge transfer resistance and the double layer capacitance fluctuate inversely during the immersion time. The fluctuations in the capacitance and resistance values reflect the variability of the active surface where corrosion process occurs and, hence, the effectiveness of passivation. In that sense, it is remarkable that in the dynamic nature of this phenomenon, passivation and depassivation can occur simultaneously on bronze surface with different extension, which indicates the growth of a resistive layer on the metal surface.

Only the first diagram recorded in CSJ present similar trend to those recorded in FJ, which illustrate the action of sulphate. After that, impedance spectra let appear two capacitive loops at high frequencies region. The first one is related to a mixed activation-diffusion control of the dissolution reaction of copper and the second could be linked to the accumulation of corrosion product layer on the

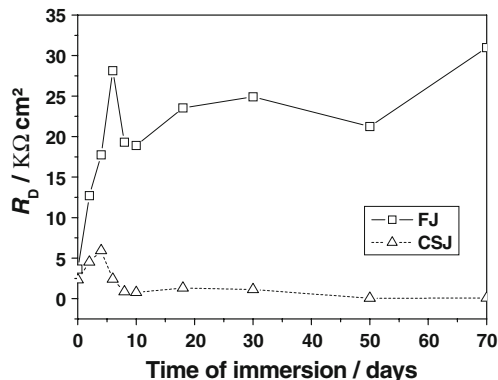


Fig. 9 Evolution of the diffusion resistance parameter (R_D) according to the time of immersion in FJ and CSJ media

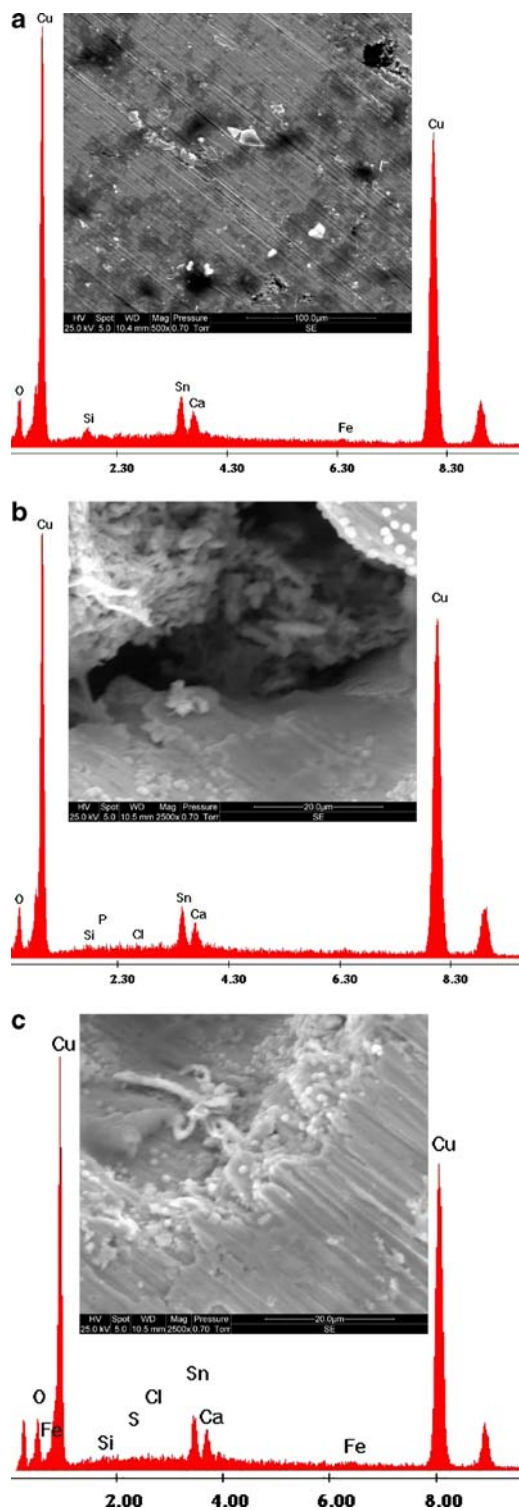


Fig. 10 Scanning electron microscopy observations and energy-dispersive X-ray spectrometry microanalysis of the corroded surface after 20 days of immersion in FJ medium

surface of bronze sample. The evolution of R_{ct} and C_{dl} , according to the immersion time, describes well the surface state of the bronze sample. These values fluctuate inversely then they undergo an important increase, which is related to

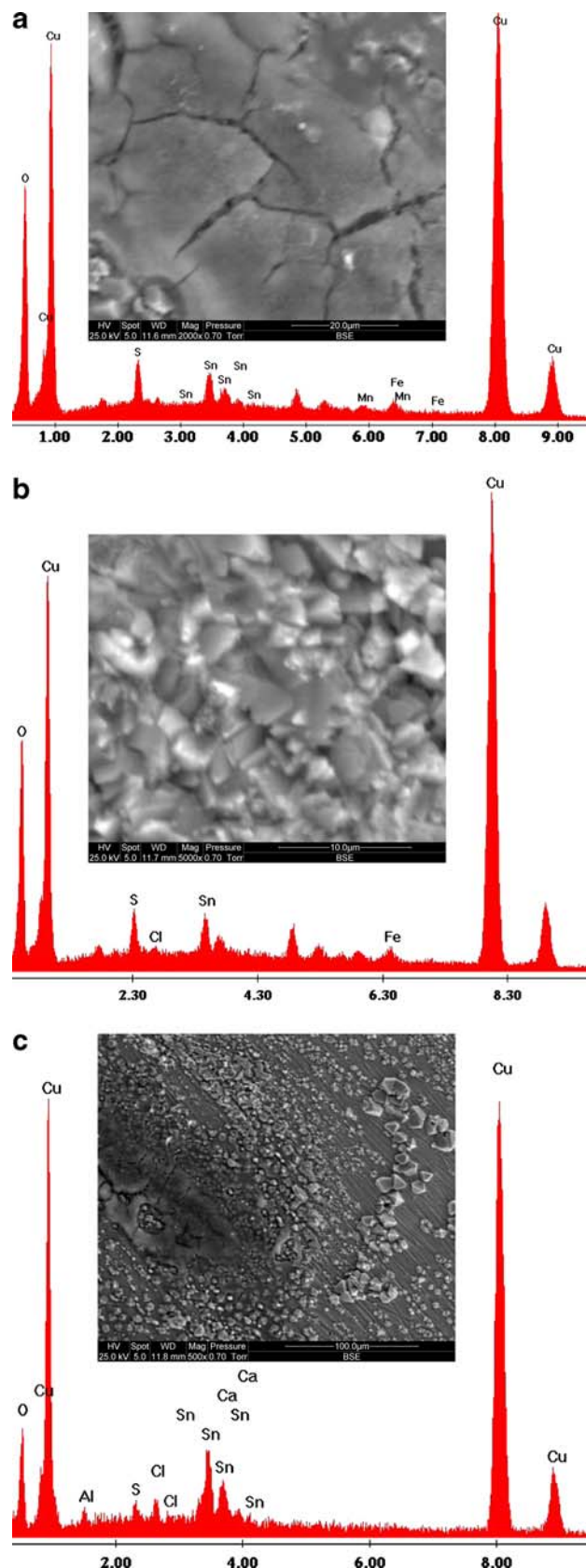


Fig. 11 Scanning electron microscopy observation and energy-dispersive X-ray spectrometry microanalysis of the corroded surface after 20 days of immersion in CSJ medium

the accumulation of corrosion products which offer a good barrier against aggressive electrolyte; after that, the corrosion process become more difficult, while the metallic surface is covered with a bronze corrosion layer “patina” which explain the capacitance decreasing and the resistance increasing (after 50 days).

SEM observation coupled with EDS analysis confirm our electrochemical results. Samples immersed in FJ are characterised by an inner corrosion layer rich with sulphate compounds and present more safe patina. More corroded surface was observed on samples immersed in CSJ. Much higher copper content in corrosion layer indicated that the copper particle was diffused into the corrosion layer due to the tendency of Cu dissolution into the corrosion layer.

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