Surface Characterization of the Corrosion Product Layer Formed on Synthetic Bronze in Aqueous Chloride Solution and the Effect of the Adding of *Juniperus Communis* Extract by X-Ray Photoelectron Spectroscopy Analysis

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Received: 19 March 2018 / Accepted: 25 July 2018 / Published online: 7 August 2018
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Abstract

The anodic surfaces formed on a synthetic bronze (Cu–10Sn) analogous to a punic material in 0.5 mol L⁻¹ aqueous chloride solution are investigated using the characterization method such X-ray photoelectron spectroscopy (XPS). The results obtained using the XPS analyses allowed to calculate the decuprification factor (f_{Cu}) and revealed the existence of the phenomenon of detannification during the corrosion process of synthetic bronze in the sodium chloride medium. We show that the copper compounds remain in the corrosion layer, acting as stabilizing specie. Using the same analysis technique XPS, the effects of a *Juniperus Communis* leaves (JC) extract on the interfacial behaviour of a Cu10Sn modern bronze has been studied. By comparing the cationic composition of the electrode without and with addition of the extract, The obtained results indicate that with the addition of the JC extract, the atomic percentage of the Cu(II) and the Sn(II) are increased which probably involves the formation of a complex in the form of (JC-Cu(+II)) and/or (JC-Sn(+II)) on the surface of the electrode. The f_{Cu} sign was also changed with the addition of the JC extract, which allows to conclude that the JC extract was concluded inhibiting tin oxidation and promoting the copper(I) dissolution.

Keywords Synthetic bronze · Corrosion · Copper–tin alloy · *Juniperus Communis* · X-ray photoelectron spectrometry

1 Introduction

Bronze alteration phenomena in different mediums have been studied in many researches [1–6]. The electrochemical behavior of archeological bronze (Cu–10Sn) in neutral aerated NaCl solution has been recently investigated through potentiodynamic measurements using a rotating disk electrode. The anodic J–E curve exhibits three main regions, that

appear closely related to the formation of different corrosion species [7]. The anodic behavior appears to be complex and corresponds to a combination of processes including a 3D growth under mixed control of layer formation reactions and the diffusion of ionic species at the interface for which chloride ions are involved.

These findings were improved by another research that characterized the anodic layers formed on Cu–10Sn bronze in 0.1 M NaCl solution [8]. In the whole anodic domain, investigations performed on a bronze rotating disk electrode (RDE) revealed the systematic formation of a uniform oxidation layer. However, XRD and XPS results revealed that the barrier layer has a complex nature, including unidentified products and different spatially distributed charged surface zones. The corrosion mechanism involves an internal oxidation of the alloy linked to a preferential dissolution of copper, namely a decuprification [8].

The corrosion of metals has many risks especially on industrial plans. The search for a solution to fight against corrosion becomes indispensable [9–24]. Unfortunately,

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synthetic products described in literature as corrosion inhibitors are toxic to humans and to the environment.

Hence, several research teams tested plant extracts as ecofriendly inhibitors [25–27]. Recently, the effect of *Juniperus Communis* (JC) extract on the inhibition of bronze corrosion in aqueous chloride solution was studied by electrochemical polarization methods [28].

The objective of this paper is to identify quantitatively, by XPS spectrometry, the species that are present on the surface of a bronze electrode (Cu10Sn) immersed in aqueous chloride medium in order to determine the specie responsible for the dissolution of the material. The second objective is to study the effect of the addition of the JC extract on the electrochemical behavior of this copper alloy.

2 Experimental

The working electrode was elaborated from a synthetic bronze (Cu10Sn), analogous to a punic material, through a procedure described in our previous work [29]. Before use, the electrode was coated with a chemically inert resin and polished with abrasive paper up to 4000 under a stream of water to avoid any change in crystal structure. It was then dipped in alcohol and rinsed thoroughly with distilled water before being immersed in electrolyte. A classical three-electrode cell was used for the electrochemical characterizations with a saturated calomel electrode as a reference and platinum wire as a counter electrode.

X-ray photoelectron spectrometry was used to determine the species present on the surface of the electrode.

The electrode was polished manually without water using abrasive paper grade 800 up to 4000 in Silicon Carbide. It was then gently dried with filtered air.

After 1 h of immersion of bronze in the solution of sodium chloride (0.5 mol L^{-1}) at a temperature of 30°C , it was rinsed with ultrapure water and dried with a filtered air before being placed under vacuum to achieve the XPS analysis.

XPS analyzes were performed with the Thermo Electron Escalab 250. Monochromated $\text{AlK}\alpha$ source was used. General spectra were recorded with an energy of 100 eV pass, high-resolution spectra with a pass energy of 20 eV. The analysis angle (angle between the surface and the direction in which the photoelectrons are analysed is 90° [30].

3 Results and Discussions

3.1 XPS Investigation of Synthetic Bronze (Cu10Sn) Immersed in a Sodium Chloride Medium (0.5 mol L^{-1})

In a previous work [31], the polarization curve was used to determine the electrochemical behaviour of a synthetic bronze electrode (Cu10Sn) analogous to archaeological bronze immersed in chloride solution (0.5 mol L^{-1}) at the temperature of 30°C for a scan rate of 10 mVs^{-1} (Fig. 1).

The anodic surface layer formed on Cu–10Sn shows that there is a layer of pseudo-passive corrosion products at the surface that is formed on Cu and Sn simultaneously.

To understand the corrosion mechanism of synthetic bronze and to link the internal oxidation of the alloy to dissolution of copper or tin, we correlate the electrochemical study with the characterisation methods such as X-ray photoelectron spectroscopy (XPS) [32, 33].

The XPS spectra for the blank electrode elements are reported in Fig. 2. The survey spectrum indicates that the main elements detected at the surface are Cu, Sn, O and C.

The atomic percentage of the compounds of the alloy present on the surface of the blank electrode are listed in the Table 1.

The high resolution spectrum Cu 2p shows a peak at 932.4 eV characteristic of metallic copper (Auger parameter value of 1851.4 eV).

The inspection of the Sn 3d $_{5/2}$ core level reveals two peaks at 484.6 and 486.1 eV. The first peak corresponds to the metallic tin and the second to the tin with an oxidation number II.

The cationic composition of the major compounds of the alloy present on the surface of the blank electrode is given in Table 2.

In Fig. 3 we illustrated the XPS spectra of the synthetic bronze immersed for 1 hour in the solution of sodium chloride (0.5 mol L^{-1}) at a temperature of 30°C . The survey spectrum indicates that the main elements detected at the surface are Cu, Sn, O and C.

The atomic percentage of the elements present on the surface of the electrode are listed in the Table 3.

The high resolution spectrum Cu 2p shows a peak at 932.3 eV of Cu + I (Auger parameter value of 1849.2 eV).

The XPS spectra display numerous broad peaks, revealing that several poorly crystallised constituents are present on the surface. We assumed here that the Sn peaks are relative to Sn(II) and Sn(IV): (Sn(IV) oxide is related to Sn 3d peak at 487.7 eV and Sn(II) oxide is related to Sn 3d peak at 486.2 eV in full accordance with the results obtained in a recent work [8].

Fig. 1 Anodic polarization curve of synthetic bronze immersed for 1 h in a solution of sodium chloride (0.5 mol L^{-1})

Table 1 The atomic percentage of the compounds of the alloy present on the surface of the blank electrode

Core level	Binding energy (eV)	Atomic percentage	Peak
C1s	284.3	20.8	C–C
C1s	285.2	3.2	C–O
C1s	287.9	3.6	C=O
Sn3d _{5/2}	486.1	4.8	Sn ²⁺
Sn3d _{5/2}	484.6	0.2	Sn
O1s	529.9	12.7	O ²⁻
O1s	531.3	13.1	OH ⁻
O1s	532.7	1	H ₂ O
Cu2p _{3/2}	932.4	40.6	Cu

Fig. 2 XPS deconvoluted spectra of the surface of a Cu–10Sn bronze

Table 2 The cationic composition of the major compounds of the alloy present on the surface of the blank electrode

Species	Atomic percentage
Cu	89.1
Sn	0.4
Sn(II)	10.5

An unusual peak appears at 489.4 eV. According to previous research, it is considered to be a peak of the tin oxychloride (Sn related to Cl) [8].

We also noticed the presence of CuCl, according to the Cu 2p_{3/2} (peak at 932.3 eV) and Cl 2p (peak at 198.3 eV). These values are close to the XPS CuCl reference core level binding energies (Cu(I) at 932.4 and Cl⁻ at 199.5 eV).

Fig. 3 XPS deconvoluted spectra of the surface of a (Cu–10Sn) bronze in NaCl (0.5 mol L⁻¹)

Table 3 The atomic percentage of the elements of the alloy present on the surface of (Cu10Sn) in NaCl 0.5 mol L⁻¹

Core level	Binding energy (eV)	Atomic percentage	Peak
C1s	284.3	13	C–C
C1s	286.2	1.9	C–O
C1s	288.1	2.4	C=O
Sn3d5/2	486.2	0.9	Sn ²⁺
Sn3d5/2	487.7	0.1	Sn
Sn3d5/2	489.4	0.1	Sn oxychloride
O1s	530.3	27.9	O ²⁻
O1s	531.6	6.1	OH ⁻
Cu2p3/2	932.3	47.6	Cu

Table 4 Composition cationic species present on the surface of the synthetic bronze immersed in the solution of sodium chloride

Species	Atomic percentage
Cu(I)	97.8
Sn(II)	1.8
Sn(VI)	0.2
Tin oxychloride	0.2

Table 5 β and f_{Cu} values of the Cu10Sn simply polished and then immersed at 30 °C in NaCl 0.5 mol L⁻¹

	(Cu/Sn) _{cdc}	(Cu/Sn) _{all}	B	f_{Cu}
Cu10Sn (after polishing)	7.56	9	0.42	2.78
Cu10Sn NaCl 0.5 mol L ⁻¹	45.08	9	0.58	-1.78

Table 4 shows the cationic composition of the major species present on the surface of the synthetic bronze immersed in the solution of sodium chloride (0.5 mol L⁻¹).

We noticed that the initial corrosion layer that formed at Eoc after 1 h of immersion in NaCl, is formed by a mixture of tin oxide(II, IV), oxychloride and copper oxide(I) [8].

XPS analysis is used to characterize the alteration process. Robbiola et al. [34–40] proposed two functions to prove the selective copper dissolution:

$$\beta = \left(\frac{(Cu/Sn)_{cdc}}{Cu/Sn_{all}} \right)$$

$$f_{Cu} = 1 - \beta = 1 - \left(\frac{(Cu/Sn)_{cdc}}{Cu/Sn_{all}} \right)$$

With

Fig. 4 β and f_{Cu} values of the Cu10Sn simply polished and then immersed at 30 °C in NaCl 0.5 mol L⁻¹

f_{Cu} : the decuprification factor

$$X = \left(\frac{Cu}{Sn} \right)_{all}$$

The ratio of the atomic fractions of copper and tin in the alloy,

$$\left(\frac{Cu}{Sn} \right)_{cdc}$$

The ratio of the atomic fractions of copper and tin in the layer of corrosion products; In order to compare our work with a previous research [8], we reported in Table 5 the values of (β and f_{Cu}) obtained for the (Cu10Sn) simply polished and then immersed in chloride solution 0.5 mol L⁻¹ after 1 h at 30 °C.

Figure 4 represents the factors β and f_{Cu} .

According to previous calculations, we note that for the corrosive solution NaCl (0.5 mol L⁻¹), the decuprification factor f_{Cu} is negative. Unlike a previous study [8], our research shows that there is no decuprification. It is rather the start of the tin detannification.

3.2 XPS Investigation of Synthetic Bronze Immersed in NaCl 0.5 mol L⁻¹ in the Presence of the JC Extract

After adding the JC extract to the NaCl solution at a temperature of 30 °C, the XPS spectra were registered (Fig. 5). The survey spectrum indicates that the main elements detected at the surface are Cu, Sn, O and C. Intensities of peaks associated to C and O are high compared to that observed before

Fig. 5 XPS deconvoluted spectra of the surface of a Cu–10Sn bronze in NaCl with JC extract

exposure to the JC extract meaning that organic species are fixed on the surface.

The atomic percentage of the species present on the surface of the electrode after the addition of the JC extract are listed in the Table 6.

The high resolution spectra of copper and tin show that copper is oxidized to Cu(I) (933.1 eV) and Cu(II)hydroxylized (934.9 eV). The small peaks at higher binding energies are satellites of Cu(II) hydroxide.

The tin mainly appears in the form of Sn(II).

Table 7 shows the cationic composition of the major compounds of the alloy present on the surface of the synthetic

bronze immersed in sodium chloride medium with the presence of JC extract.

By comparing the cationic composition of the electrode with and without adding the extract, it can be concluded that the extract JC generates increasing atomic percentage of Cu(+II) and Sn(II), which probably involves the formation of a complex in the form of (JC-Cu(+II)) and/or (JC-Sn(+II)) on the surface of the electrode.

After the addition of the JC extract, the f_{Cu} becomes positive with a value of 0.23. The JC extract blocks the dissolution of tin and supports the departure of copper (decuprification).

Table 6 Atomic percentage of the species present on the surface of the synthetic bronze immersed in the solution of sodium chloride (0.5 mol L^{-1}) with the presence of JC extract

Core level	Binding energy (eV)	Atomic percentage	Peak
Cu2p3/2	933.1	1.2	Cu(I)
Cu2p3/2	934.9	3.1	Cu(II)hydroxyde
Cu2p3/2	943.4		Satellites of Cu(II) hydroxide
Cu2p3/2	939.1		Satellites of Cu(II) hydroxide
C1s	284.2	38.7	C–C
C1s	285.9	25.3	C–O
C1s	287.5	3.9	C=O
O1s	531.3	11.0	O ²⁻
O1s	532.8	16.5	OH ⁻
Sn3d5/2	486.6	0.3	Sn ²⁺

Table 7 Composition cationic species present on the surface of the synthetic bronze immersed in the solution of sodium chloride (0.5 mol L^{-1}) with the presence of JC extract

Species	Atomic percentage
Cu(I)	26.1
Cu(II)	67.4
Sn(II)	6.5

4 Conclusion

The purpose of this paper is to characterize the species present on the surface of the bronze electrode in a chloride solution (0.5 mol L^{-1}) with and without the addition of the JC extract, using the X-ray photoelectron spectrometry investigations.

XPS semi quantitative characterisation revealed that the cationic composition at the material surface when submitted to the aggressive medium was 97.3, 1.8 and 0.2% respectively for Cu(I), Sn(II) and Sn(IV). Furthermore, the bronze surface composition was 6.5, 26.1 and 67.4% respectively for Sn(II), Cu(I) and Cu(II) when the JC extract was added.

XPS analyzes show the existence of the phenomenon of detannification during the corrosion process of bronze in the sodium chloride solution.

The decuprification factor f_{Cu} was -1 and 0.23 respectively with and without the plant addition. We concluded that the JC extract inhibits tin oxidation and promotes Cu(I) transformation.

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