BRONZE CORROSION IN AQUEOUS CHLORIDE MEDIUM

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Abstract: The electrochemical behaviour of bronze alloy (Cu10Sn) corrosion in aqueous chloride solution was studied by electrochemical polarization methods. Results showed that the surface's compounds were mainly (hydroxide) oxides of tin and copper, incorporating very low amounts of chlorides. The variation of three experimental factors such as the sweep rate, the chloride concentration and the temperature allow us to deduce the activation thermodynamic parameters of this process.

Keywords: Synthetic bronze, Copper-tin allow, Analytical and electrochemical characterizations, Corrosion

INTRODUCTION

Bronzes (Cu–Sn based alloys) are very interesting specimens for improving our understanding of corrosion phenomena in natural environments (soil, sea, atmosphere...). As they were produced since more than five millennia, these materials reveal inestimable information for investigating not only long term corrosion but also the formation of corrosion layers (natural patinas) exhibiting some passive behaviour [1].

Many studies have shown that electrochemical techniques combined to complementary investigations are powerful methods for understanding the formation of bronze patinas.

Investigation of the electrochemical behaviour of Cu–10Sn (wt.%) alloy has been conducted in aerated aqueous chloride solutions and compared to that of pure Cu and Sn. Cathodic and anodic bronze behaviours have been investigated in function of the chloride concentrations (0.1–0.001 M),the rotation speed of the electrode and the potential sweep rate after 1-h immersion time in open circuit conditions. At the corrosion potential, the corrosion behaviour appears determined by the charge-transfer controlled reduction of oxygen and the mixed charge- and mass-transfer controlled electrodissolution [2].

The objective of this paper is to study the electrochemical behaviour of a synthetic bronze (Cu–10Sn) in 0.5 mol.L^{-1}chloride solution, it has been chosen because its composition is almost equivalent to that of seawater. Cathodic and anodic bronze behaviours have been investigated in a chloride medium close to the open circuit potential after one hour of immersion time.

To better understand the mechanism of bronze corrosion in the sodium chloride solution, influence of different parameters such as the scan rate, chloride concentration and temperature on the Taffel region of the polarization curves were also studied.

EXPERIMENTAL DETAILS

The working electrode was elabored from a synthetic bronze (Cu10Sn) through a procedure described in our previous work [2]. Before use, it has been embeded with a

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chemically inert resin and polished with abrasive paper up to 4000 under a stream of water to avoid crystal structure. It transported in alcohol and rinsed completely with distilled water before being immersed in the corrosive electrolyte.

Chloride corrosive electrolytes were prepared when dissolving appropriate amounts of analytical quality reagent in distilled water. The pH was for all solutions equal to 7 without further adjustments.

A classical three-electrode cell was used for the electrochemical characterizations with a saturated calomel electrode as reference and platinum wire as counter electrode. Experiments were conducted on a Voltalab 80. Voltmaster 4 software was used for instrumentation control and data treatment.

All the results are given with respect to the saturated calomel electrode.

RESULT AND DISCUSSION

1. Voltametric behaviour of synthetic bronze in chloride medium

1.1. Anodic behaviour of synthetic bronze

Fig. 1 showed the current-potential anodic curve for synthetic bronze after an hour of immersion in 0.5 mol.L^{-1} chloride solution at a scan rate of 10 mV s^{-1}.

The polarization curve of modern bronze has an area of activity which extends the corrosion potential up to 60 mV/SCE, which corresponds to the oxidation peak, where the compounds formed on the surface of bronze are those formed on Cu and Sn simultaneously: CuCl, $SnCl_2$ and/or Sn(OH) Cl, $SnCl_4$ and/or $Sn(OH)_xCl_{4-x}$[3].

In addition, the current density of the alloy shows a slight fall to stabilize at the stationary state current Iss.

The effect of the passivating film is probably due to the transformation of nantokite in cuprite, while aggressive anions are Cl-complexed tin according to the reaction equations (1) and (2) [3-4]

$$2\,CuCl + H_2O \rightleftharpoons Cu_2O + 2\,H^+ + 2\,Cl^- \qquad (1)$$

$$Sn(OH)_xCl_{4-x} + x\,CuCl \rightleftharpoons SnCl_4 + {}^{x}/_{2}\,Cu_2O + {}^{x}/_{2}\,H_2O \qquad (2)$$

avec $1 \leq x \leq 4$.

1.2. Cathodic behaviour of synthetic bronze

Cathodic polarization curves of the (Cu10Sn), immersed for one hour at 30°C in 0.5 molL^{-1}NaCl are given in Fig. 2 at scan rate of 10 mV.s^{-1}.

The cathodic curve characterized by the presence of the cathodic peak (1c) to -1117mV/ECS with a maximum current of -0.7 mA cm^{-2} was attributed to the reduction of tin species by the following transformation (equation 3)

$$Sn\,(II) \rightarrow Sn\,(0) \qquad (3)$$

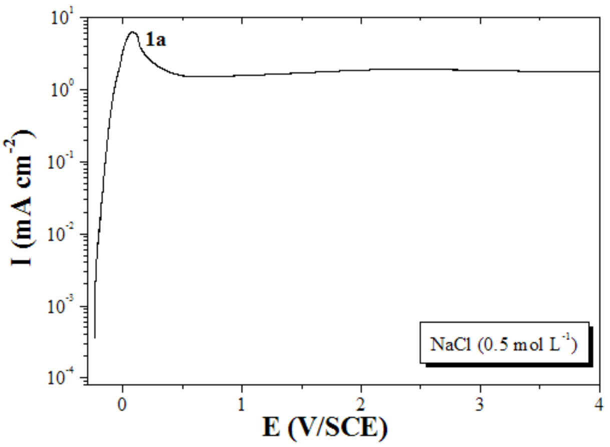

Figure1: Polarization anodic curve of synthetic bronze immersed at 30°C for one hour in a solution of sodium chloride 0.5 mol L^{-1} at a scan rate 10 mV s^{-1}.

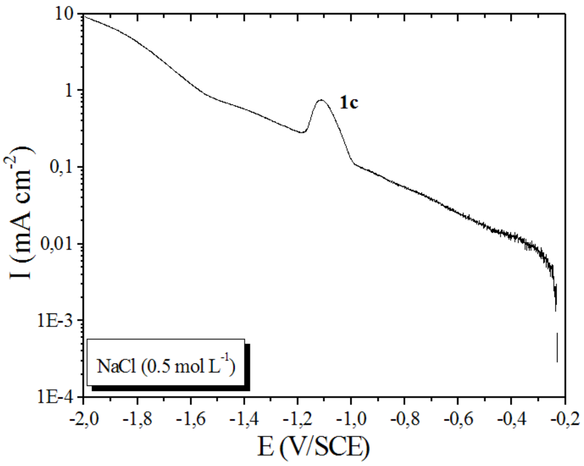

Figure2: Polarization cathodic curve of synthetic bronze immersed at 30°C for one hour in a solution of sodium chloride 0.5 mol L^{-1} at a scan rate 10 mV s^{-1}

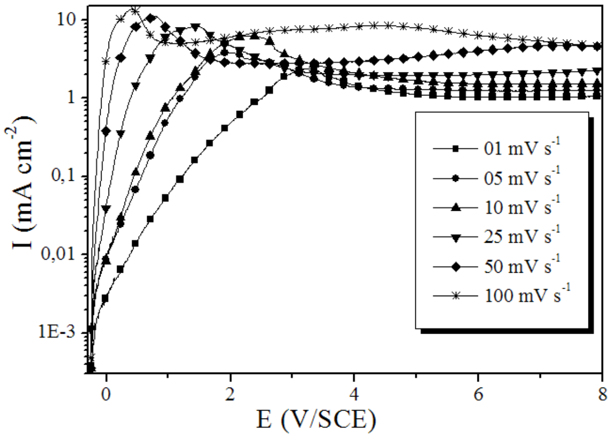

Figure 3: Variation with the scan rate of Cu10Sn immersed at 30°C for one hour in NaCl 0.5 mol L^{-1}

2. Scan rate effect on the voltametric behaviour of the modern material

2.1. Anodic behaviour of synthetic bronze

Voltammograms, swept from Eo.c to 4V were recorded for the bronze alloy immersed in 0.5 M chloride electrolyte at various sweep rates in the following descending order: 100, 50, 25, 10, 5 and 1 mV s^{-1} (Fig. 3).

The obtained results show a decrease on the scan rate leading to a decrease in the current density all through range.

A linear relation is obtained between the peak current densities of the sweep rate with a regression coefficient of about 0.97 (Fig. 4).

These data are in accordance with a “pore resistance model” where the layer formed at peak spreads over the electrode surface until small pores remained [3-5-6]. Diffusion through the pores then controls the rate of the patina formation.

Moreover, the results are in good agreement with the model of Müller and Calandra [7-9]. In this model the peak current is given by the equation of the patina formation (equation4) [8-9].

$$I_p = \left(\frac{nF\rho\kappa}{M}\right)^{1/2}(1-\theta_p)v^{1/2} \qquad (4)$$

With

Ip :the current and the anodic peak potential;

n: the number of electrons exchanged;

F: Faraday constant;

ρ: the film density products from the surface;

k: the specific conductivity of the solution within the pores of the film;

θ p : the cover factor of the surface;

The formed layer at the peak is due to the products reaction which covers the surface leadings to an increase in the ohmic resistance at the pores [8-9]

In order to determine the relative rate of surface oxidation of the material, a plot of the stationary state current (Iss) is obtained at different potentials (3500 mV, 3750 mV and 4000 mV) versus the sweep rate which was constructed (Fig. 5).

The current density increased exponentially in function of the sweep.

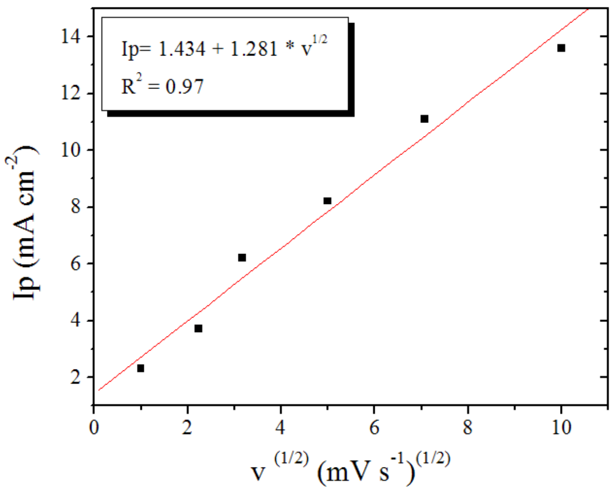

Figure 4: Scanning rate effect an anodic peak curren

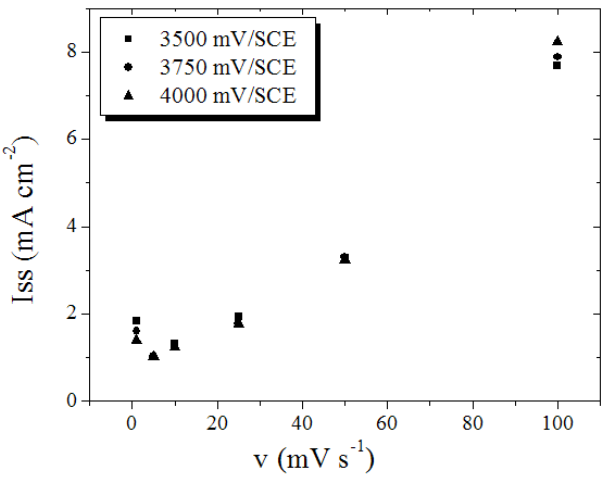

Figure 5: Scanning rate effect in Iss

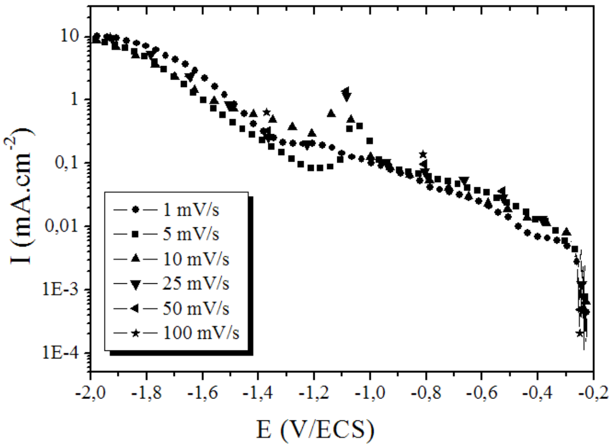

Figure 6: Variation with the scan rate of Cu10Sn immersed at 30°C for one hour in NaCl 0.5 mol L^{-1}

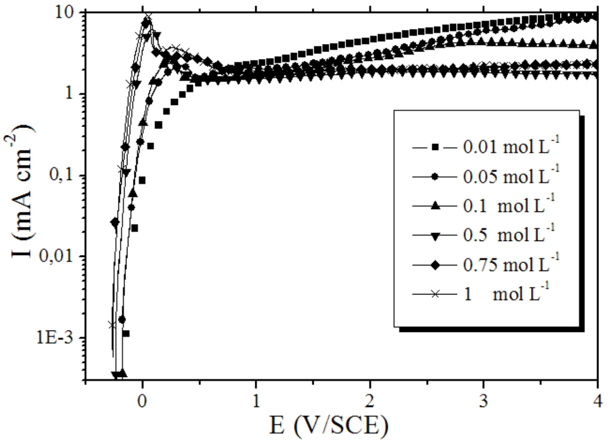

Figure 8: Variation with the [Cl$^-$] of Cu10Sn immersed at 30°C for one hour in NaCl with a scan rate 10mV.s^{-1}

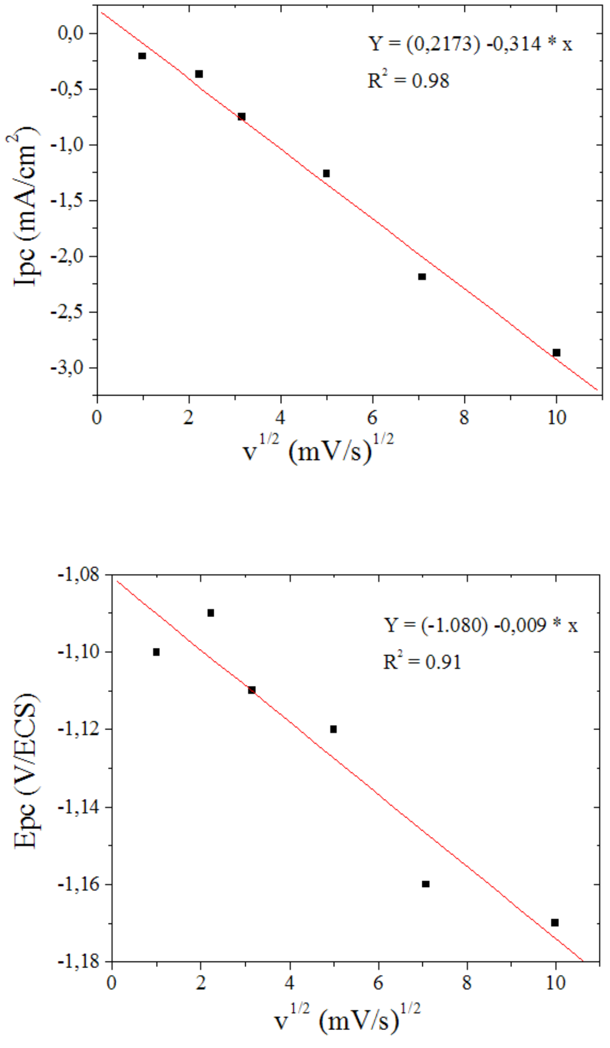

Figure 7: Effect the scanning rate on the currents (a) and the potentials (b) of the cathodic peak

2.2. Cathodic behaviour of synthetic bronze

Fig. 6 summarize the I-E curves for the Cu10Sn bronze immersed at 30°C in 0.5 M chloride electrolyte at various scan rates :100, 50, 25, 10, 5 and 1 mV.s^{-1}

Linear dependence is observed between the cathodic peak currents, potentials and the square root of the scan rate (Fig. 7a and b). Reduction of surface layer seems to be under diffusion control.

3. Effect of the chloride concentration on the voltammetric behaviour of the synthetic bronze

3.1. Anodic behaviour of synthetic bronze

The influence of chloride concentration of the Cu- 10Sn alloy is illustrated in Fig. 8. I-E curves were swept from Eo.c to 4000 mV at a scan rate of 10 mV s^{-1}.

It was found that the decrease of the concentration of chloride ions tended to move the open circuit potential to the anodic values as well as a decrease in the intensity of the current.

Thus, the contribution of chloride ions causes an increase in the anodic reaction and dissolution of the material.

We noted also that the intensity of the anodic peak decrease when the amount of chloride diminish, it takes a minimum value for a chloride concentration equal to 0.01 mol. L^{-1}.

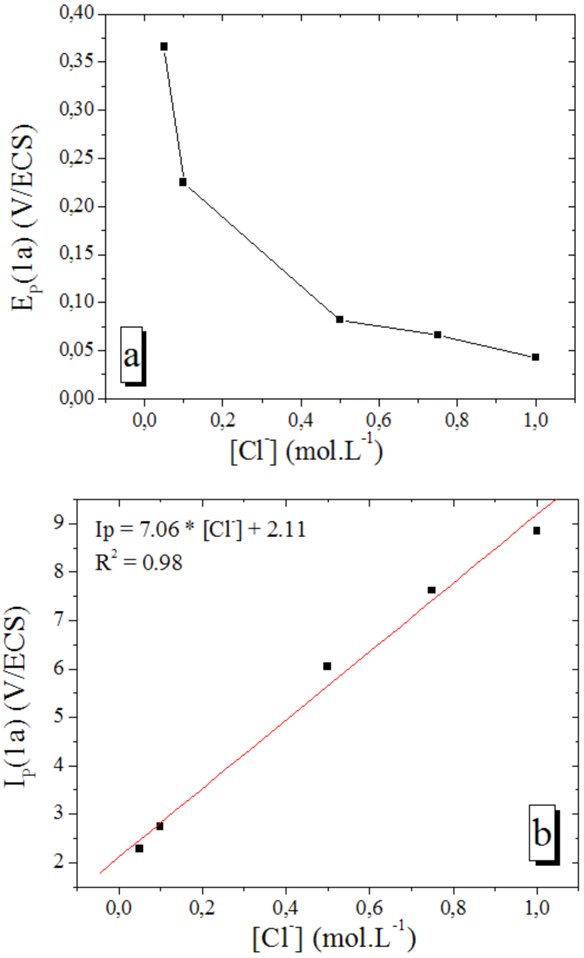

Figure 9: Effect of the concentration on the the potentials (a) and the currents (b) of the two cathodic peaks

Anodic peak (1a) potentials are shifted to negative range when the anion concentration increases. (Fig.9)

As expected a linear dependence was observed between peak currents and [Cl$^-$] (Fig. 9b). The Nicholson-Shain criteria being satisfied, the layer growth is under anionic diffusion control [10-11]

$$I_p = k\ n^{3/2}\ C\ D^{½}\ v^{½} \qquad (5)$$

with :

$$k = 0{,}446F\left(\frac{F}{RT}\right)^{½}$$

k : Randles – Sevick constant ;

n : the number of electrons exchanged ;

C : the concentration of solute at the interface ;

D : the diffusion coefficient;

v : the scan rate ;

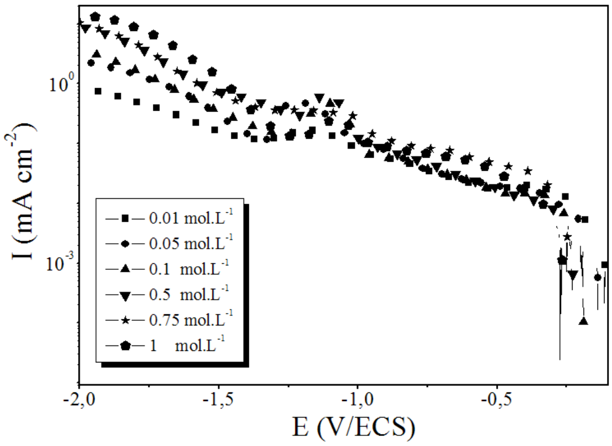

Figure 10: Variation with the [Cl$^-$] of Cu10Sn immersed at 30°C for one hour in NaCl with a scan rate 10mV.s^{-1}

3.2. Cathodic behaviour of synthetic bronze

The influence of chloride concentration on the voltammogram of the Cu- 10Sn alloy is illustrated in Fig. 10. I-E curves were swept

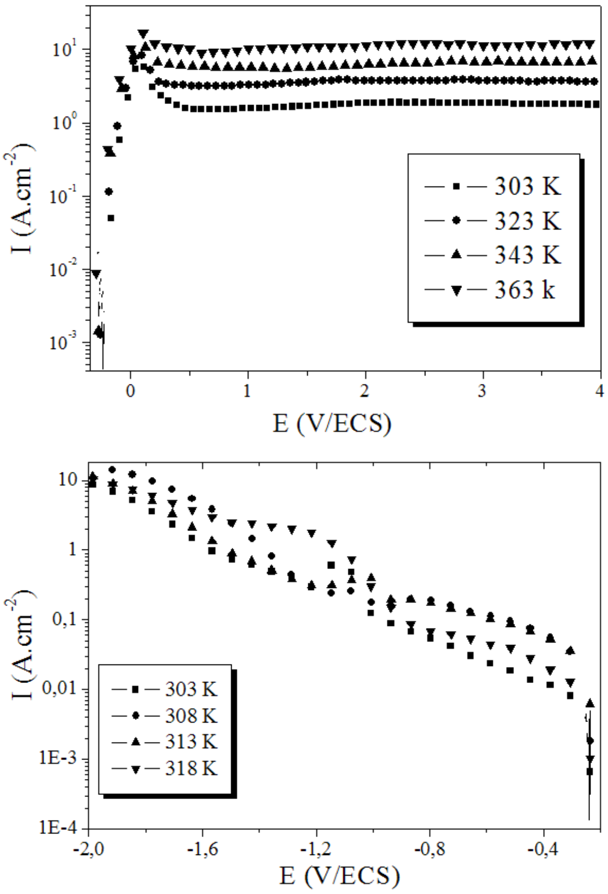

Figure 11: Variation with the temperature of Cu10Sn (a: anodic curves / b: cathodic curves) immersed for one hour in NaCl 0.5 mol L^{-1} with scan rate 10mV.s^{-1}

from Eoc to -2000 mV at a scan rate of 10 mVs^{-1}.

It appears that the decrease in concentration moved the open circuit potential of the material to anodic values after one hour of immersion and the decrease of the anodic current when [Cl^-] diminish.

3.3. Effect of the temperature on the voltammetric behaviour of the synthetic bronze

To determine the influence of temperature (30°C to 45° C) on the behaviour of the interfacial material after one hour of immersion in a chloride electrolyte. The curves IE (anodic and cathodic) were plotted. The results are reported in Fig. 11.

Curve Ln (Icorr) in function of the reciprocal of absolute temperature (Fig. 12a) gives an affine line. This result is in agreement with the Arrhenius law [12]

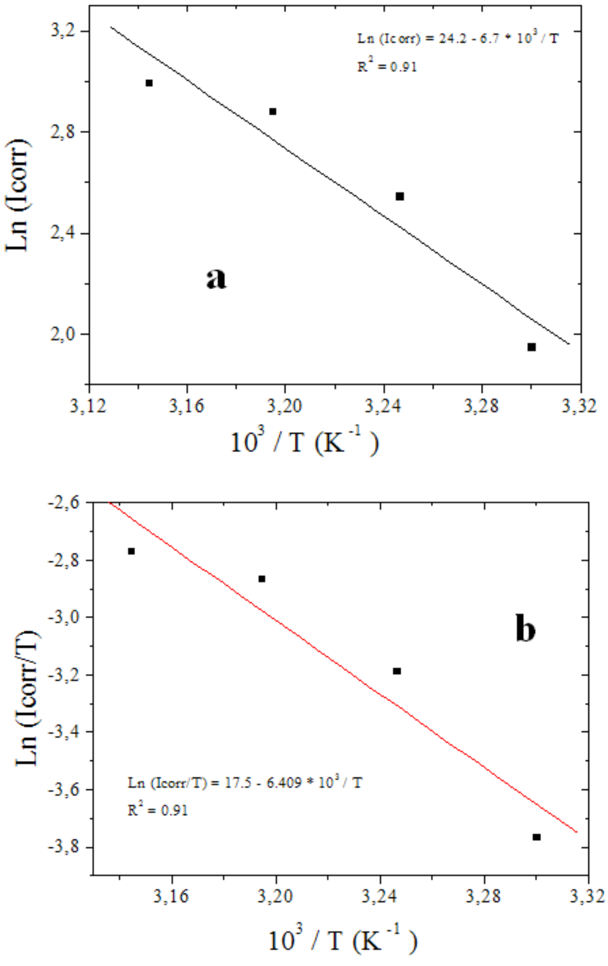

Figure 12: Ln Icoor (a) and ln (Icorr/T) (b) evolution

$$I_{corr} = A \exp\left(\frac{-Ea}{RT}\right) \qquad (6)$$

with:

A : pre-exponential factor;
Ea: activation energy;
R : gas constant;
T : absolute temperature.

Thus, the activation energy of the process could be determined and it is equal to 55.7kJ.mol^{-1}.

To characterize the activation kinetics of corrosion of bronze synthesis, we attempted to verify the Eyring law.

$$I_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(\frac{-\Delta H^*}{RT}\right) \qquad (7)$$

R : gas constant;
T : absolute temperature;
N : Boltzmann's constant;
h : Planck's constant;
ΔH^* : the activation enthalpy;
ΔS^* : the entropy of activation.

As reported in Fig.12, b $\mathrm{Ln}\left(\frac{Icorr}{T}\right)$ varies linearly with 1/T.

The slope corresponds to $\left(\frac{-\Delta H^{\neq}}{R}\right)$ and the intercept is equal to $\left(\mathrm{Ln}\left(\frac{R}{Nh}\right) + \frac{\Delta S^{\neq}}{R}\right)$

Thus, those $\Delta H^{\#}$ and $\Delta S^{\#}$ could be calculated (Tab. I)

The positive sign of ΔH^* reflects the endothermic nature of the dissolution process.

Table I: Values the quantities $\Delta H^{\#}$ and $\Delta S^{\#}$ for the system

ΔH^* (kJ mol^{-1})	ΔS^* (J mol^{-1} K^{-1})
53.3	-945.5

The negative sign of ΔS^* imply that the activated complex in the rate-determining step represents the association rather than dissociation, meaning that a decrease in disorder takes place, going from reaction to the activated complex [13, 14].

CONCLUSION

The aim of the paper was to develop our understanding on the electrochemical behaviour of (Cu10Sn) in 0.5 M neutral chloride solution.

The anodic surface layer formed on Cu–10Sn show that it is characterized by compounds formed on Cu and Sn simultaneously. Its reduction seems to be under diffusion control.

The variation of the temperature and the chloride concentration allowed the verification of the Arrhenius and Eyring laws.

The thermodynamic properties show the endothermic nature of the dissolution process and its tendency to decrease the molecules disorder.

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