

Corrosion inhibition of bronze, copper and iron in urban-marine media by 3-amino 1,2,4-triazol

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Abstract

The 3-amino 1, 2,4-triazol, refereed as (ATA), was tested as inhibitor for different materials (copper, iron and bronze) corrosion in urban-marine solutions by electrochemical polarization methods and weight loss measurement. Results obtained in this study reveal that ATA is a good inhibitor and the potentiodynamic polarization studies clearly show that ATA is a mixed-type inhibitor for bronze, cathodic inhibitor for iron and anodic inhibitor for copper. The inhibition efficiency of ATA increases with the increase of inhibitor concentration and reaches an optimum value (up to 90 %) at 10^{-2} M in urban-marine solution for the different substrates.

The SEM-EDX analysis of the protective layer of ATA after corrosion experiments shows that the inhibitor prevents metal corrosion by the formation of a protective layer and the adsorption of the inhibitor on the surface.

Keywords: Bronze; copper; iron; electrochemical properties; surface analysis; Corrosion; triazole.

The archaeological objects exposed in museums have often been adversely affected due to spontaneous aggressiveness of the environment of museums. Now, the objects buried for centuries in the ground or in the aqueous environment have gained certain stability with this environment. The corrosion processes were so slow that they became negligible. However, after excavation, the sudden change of environment and sometimes exposure in a corrosive atmosphere such as marine and/or urban provokes the restart of the corrosion. The protection of the metallic objects of cultural heritage becomes of a great importance [1-13].

Among the methods used to enhance the stability of the materials is the inhibition that delays the corrosion rate by acting in several ways depending on the nature of the material and the inhibitor. In general, organic compounds containing polar groups including nitrogen, sulfur, phosphorus, and oxygen, and heterocyclic compounds with polar functional groups and conjugated double bonds [14–18] have been reported as good corrosion inhibitors. The inhibiting action of these organic compounds is usually attributed to their interactions with the metal surface via their adsorption [19-21]. In most of the cases, the interaction with the metal is favored when the inhibitor is a planar conjugate molecule with a high p/lone-pair electron density [22–25]. However, the adsorption of an inhibitor on a metal surface depends on the nature as well as the surface charge of the metal, the adsorption mode, the inhibitor's chemical structure, and the type of the electrolyte solution [26].

Many authors have investigated the corrosion control of copper, iron and steels in various media using large numbers of organic and inorganic compounds [27 - 41]. Many works can be found in the literature about inhibitor properties of aminotriazole (ATA) and its action [42-44]. They have established that this molecule acts by formation of a tridimensional film as an organic revetment.

The aim of the present work is to study the inhibiting efficiencies of aminotriazol (ATA) in corrosion process of bronze, copper and iron in urban-marine medium. The investigation is performed using electrochemical methods, weight loss measurements and the surface analysis.

2. Experimental procedure

2.1. Materials and solution

Copper (99% wt), iron (99% wt) or bronze (its chemical compositions was given in table 1)

were used as the working electrode. Metal electrode for corrosion studies have a surfaces area of 0.785 cm² for bronze, 1.1 cm² for iron and 1.4 cm² for copper. These samples were first mechanically polished using SiC paper in successive grades from 500 to 1200, washed with deionized water thoroughly, degreased with absolute ethanol and dried.

We used for the corrosion tests, a solution constituted of 0.2 g. L⁻¹ of Na₂SO₄ + 0.2 g. L⁻¹ of NaHCO₃ + 0.2 g. L⁻¹ of NaCl. The pH was adjusted to 3 by the addition of HCl. This middle represents the environment of urban-marine zone. For the inhibition study, we used an organic molecule; the aminotriazole (ATA) of chemical formula C₂H₄N₄.

Table 1: Composition of the bronze (% wt).

Element	Fe	Ni	Al	Cu
% wt	4.2	8.97	8.66	78.26

2.2. Weight Loss Measurements

Gravimetric experiments were carried out in a double glass cell. The weight loss (in mg cm⁻²) was determined at different immersion times by weighing the cleaned samples before and after hanging the sample into 30 mL of the corrosive solution in the absence and presence of various ATA concentrations. At the end of the tests, the specimens were carefully washed in distilled water and dried in hot air and then weighted. All tests have been performed at room temperature in aerated solution. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed calculation of inhibition efficiency of our extract according to the following equation:

$$E\% = \left(\frac{W^\circ - W}{W^\circ} \right) \times 100$$

Where W and W[°] are the weight loss of alloy samples obtained in corrosive solution in the presence and in the absence of inhibitor, respectively.

2.3. Polarization Measurements

Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell, containing 100mL of electrolyte at room temperature. A standard three-electrode cell was used with Platinum electrode as a counter electrode and a saturated calomel electrode

(SCE) as a reference electrode. All potentials are reported vs. SCE. Before each Tafel experiment, the working electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 60 min. After this time, the potentiodynamic Tafel measurements were started from E_{corr} to the anodic or cathodic direction in the absence and in the presence of inhibitor molecule (ATA), with a scan rate of 2 mVs^{-1} . For polarisation measurements, a potentiostat Voltalab 301 PGZ monitored by a PC computer and Voltamaster 4.0 software were used for run the tests, collect and evaluate the experimental data. During each experiment, the test solution was mixed with a magnetic stirrer.

The inhibition efficiency (E %) was calculated using the following equation:

$$E\% = \left(\frac{I^{\circ} - I}{I^{\circ}} \right) \times 100$$

Where I° and I are, respectively, the corrosion current densities obtained in corrosive media in the absence and the presence of inhibitor.

2.4. Surface and solution analysis

The surface morphology and chemical analysis of alloy specimens after polarization measurements in urban-marine media in the absence and the presence of inhibitor (ATA) were studied using a scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) techniques. X-Ray Diffraction measurements were performed using a XRD 3003-TT diffractometer equipped with secondary monochromator and with a Cu $K\alpha$ radiation source ($K\alpha_1 = 1.54$) in order to reveal the nature of phases. A goniometer θ - θ (vertical) was used for XRD studies. A scanning electron microscopy (Quanta 200 Fci Company with EDS) was coupled to these characterizations to qualify corrosion layers and morphologies.

Spectroscopy induction coupled plasma was used to analyze the solution. The calibration is made in the studied solution in order to eliminate the effect of matrix.

3. Results and discussion

3.1. Potentiodynamic tests

Polarization measurements have been carried out in order to gain knowledge concerning the kinetics of the anodic and cathodic reactions for different materials in the absence and

presence of ATA molecule in urban-marine media. The obtained polarization curves of materials in urban – marine solution without and with different ATA concentrations are shown in Fig. 1. The values of the electrochemical kinetic parameters (corrosion potential (E_{corr}), corrosion current density (I_{corr})), determined from these experiments are summarized in Table 2. They show that the addition of the inhibitor decrease the attack of the metal working electrode.

The corrosion potential (E_{corr}) in solutions containing inhibitor is shifted towards more positive values with the increase of its concentration (Table 2). The addition of ATA had influence on anodic and/or cathodic part depending on the nature of material. The corrosion current decrease is more pronounced when the concentration ATA increases. Compared to the blank samples (Fig. 1) the cathodic curves indicate that all the cathodic polarization curves for iron and bronze in the absence and presence of ATA are parallel which suggests that the hydrogen evolution is activation controlled and the presence of inhibitor decrease the current without changing the mechanism of reduction reaction [45, 46].

For iron, no remarkable influence on the anodic part is observed but the addition of ATA substantially reduces the cathodic current density. The efficiency rate obtained from the polarization curves reached a maximum value of 91% for concentration of 10 mM in ATA.

For copper (Fig 1b), the anodic curves of the copper electrode in the urban-marine solution shift obviously to the direction of current reduction as adding the ATA, which implies that the organic compound can suppress the anodic reaction (copper dissolution). Based on the marked decrease of the anodic current densities upon introducing the inhibitor in the aggressive solution, this inhibitor is considered as an anodic inhibitor for copper.

For bronze (Fig1c and 1d), we note the reduction of the cathodic and anodic current densities. This means that the addition of ATA reduces the anodic dissolution and also retards the cathodic hydrogen evolution reaction.

Fig.2 presents the variation of inhibitor efficiency versus the logarithm of the concentration in inhibitor. It results from the linear dependence observed that the adsorption of ATA compound on the surface of alloy follows an isotherm of Temkin:

$$\theta = \frac{RT}{q_0 \alpha} \ln A_0 C$$

Where θ is the coverage of an electrode surface by an adsorbed inhibitor, q_0 the adsorption temperature, α and A_0 the constants of the system at constant temperature.

Table 2: Electrochemical parameters of iron, copper and bronze in urban-marine media in the presence of different concentrations of ATA.

	Cathodic part				Anodic part		
alloy	[ATA] (mM)	E_{cor} (mV/ECS)	i_{cor} ($\mu A.cm^2$)	E (%)	E_{cor} (mV/ECS)	i_{cor} ($\mu A.cm^2$)	E (%)
Iron	0	-627	829	-			
	0.1	-611	311.5	62.4			
	1	-582	184	77			
	10	-543	74.8	91			
Copper	0				-92	863	-
	0.1				-20	701	19
	1				-63	164	81
	10				-82	64.7	92.5
Bronze	0	-132	135	-	-138	897	-
	0.1	-50	58.9	56.3	-45	522	41.8
	1	-140.8	46.5	65.5	-93	330	63.2
	10	-141	40.9	69.7	-136	131	85.4

3.2. Dissolution rate in the passive state

Copper and bronze dissolution rate were studied at +600mV/ECS, in urban-marine media in the absence and in the presence of different concentration of ATA molecule (Fig. 3). Current

densities decrease quickly and take very low values. In the presence of 10mM of ATA, the dissolution rate in the passive state is the lowest and the rate of formation of passive film is highest (stationary state is achieved after few minutes). The decrease of the dissolution kinetics in the presence of ATA suggested the film became less porous and more protective owing the introduction of ATA in the film.

3.3. Gravimetric measurements

The gravimetric measurements corroborate the electrochemical results. The inhibitor efficiency and the corrosion rate were calculated by weight loss measurements for an immersion period of 24h or 7 days and varying concentrations in ATA. Corresponding data are given in Table 3.

Examination of Table 3 shows that the addition of ATA reduces the corrosion rate of alloys. For copper and 10mM of ATA, the immersion time influences the corrosion rate without changing the efficiency of inhibitor. For the iron, we noted the formation of a thick film on the surface that induces an increase the mass of sample after immersion period of 24H. The best efficiency is obtained for 10mM of ATA.

Table 3: Inhibitory efficiency and corrosion rate determined by weight loss measurements after 24 hours and 7 days of immersion period.

	Time	24H		7 days	
alloy	[ATA] (mol/L)	corrosion rate (mg.cm ⁻² .h ⁻¹)	E%	Corrosion rate (mg.cm ⁻² .h ⁻¹)	E%
Iron	0	0.022	-		
	10 ⁻⁴	0.011	50		
	10 ⁻³	0.011	50		
	10 ⁻²	0.025	-		
Copper	0	3.4.10 ⁻²	-	6.6.10 ⁻³	-
	10 ⁻⁴	1.7. 10 ⁻²	50	4.96.10 ⁻³	24.8
	10 ⁻³	0.6. 10 ⁻²	82.3	2.48.10 ⁻³	62.4
	10 ⁻²	0.5. 10 ⁻²	85.3	0.9610 ⁻³	85.4
Bronze	0			4.9.10 ⁻³	-
	10 ⁻⁴			2.7.10 ⁻³	44.9
	10 ⁻³			1.57.10 ⁻³	67.9
	10 ⁻²			0.45.10 ⁻³	90.8

3.4. Surface analysis by SEM-EDS

For iron, the observation of the surface after immersion in urban-marine solution in the presence of 10mM of ATA for 7 days (Figure 4-b), shows the formation, on the surface of iron of a more homogeneous film that covers the entire surface. The EDS analysis shows the

presence of peaks attributed to nitrogen and carbon due to the adsorption of inhibitor on the surface. The XRD patterns of the iron after immersion in urban-marine media for 168h indicates that oxy-hydroxide of iron have formed at the surface.

We observed the surface of copper electrodes after immersion in the urban-marine media in the absence and presence of ATA for 7 days (Fig. 5). In the presence of ATA, SEM micrograph (Figure 5-b) shows a uniform surface and did not present any corrosion form. We note the formation of a protective layer over the surface of copper. EDS analysis shows the presence of carbone and nitrogen and the absence of chloride on the surface. In the absence of ATA, The XRD patterns of the copper after immersion in urban-marine media for 168h indicates that CuO have formed at the surface. EDS analysis shows the presence of chloride adsorbed on the surface.

SEM micrograph performed on the bronze electrode after 7 days of immersion in the corrosive solution in the presence of 10 mM ATA (Figure 6-b) shows the surface degradation significantly less than that observed in the absence of inhibitor (Figure 6-a).

Analyze of each solution by ICP after 7 days of immersion period allows us to calculate the corrosion rate of alloys in corrosive medium (Table 4). These results are in good agreement with the obtained value of corrosion rate obtained by weight loss measurement.

Table 4: Corrosion rate of alloys calculated using the ICP analysis of corrosive solution containing 10mM of ATA and after immersion of alloys for 7 days period at room temperature.

Alloy	Iron	Copper	Bronze
Corrosion rate $\text{mg.cm}^{-2}.\text{h}^{-1}$	$1.1 \cdot 10^{-2}$	$5.5 \cdot 10^{-3}$	$4.7 \cdot 10^{-3}$

4. Conclusion

Electrochemical study and weight loss measurements showed that ATA acted as efficient corrosion inhibitors of bronze, copper and iron in urban-marine solution. The maximum inhibition efficiency reached exceeded 85%.The observed protecting effect of this inhibitor

was affected by the nature of alloy. For 10mm of AFA, the inhibition efficiency did not change significantly with increase in the immersion period. The inhibitor tested act by adsorption on the surface leading to the formation of protective inhibitory films.

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Figure 1: Polarization curves of iron (a), copper (b) and bronze (c and d) recorded in urban-marine media at different concentrations of ATA.

Figure 2 : Variation of inhibitor efficiency vs. the logarithm of ATA concentration

Figure 3: The passive current transients of copper (a) and bronze (b) in urban-marine solution in the absence and presence of different concentrations of ATA. Applied potential=600mV/SCE

Figure 4: micrograph of the electrode of iron after immersion in urban-marine media without (a) and with 10mM of ATA (b).

Figure 5: micrograph of the electrode of copper after immersion in urban-marine media without (a) and with 10mM of ATA (b).

Figure 6: micrograph of the electrode of bronze alloy after immersion in urban-marine media without (a) and with 10mM of ATA (b).

Table 1: Composition of the bronze (% wt).

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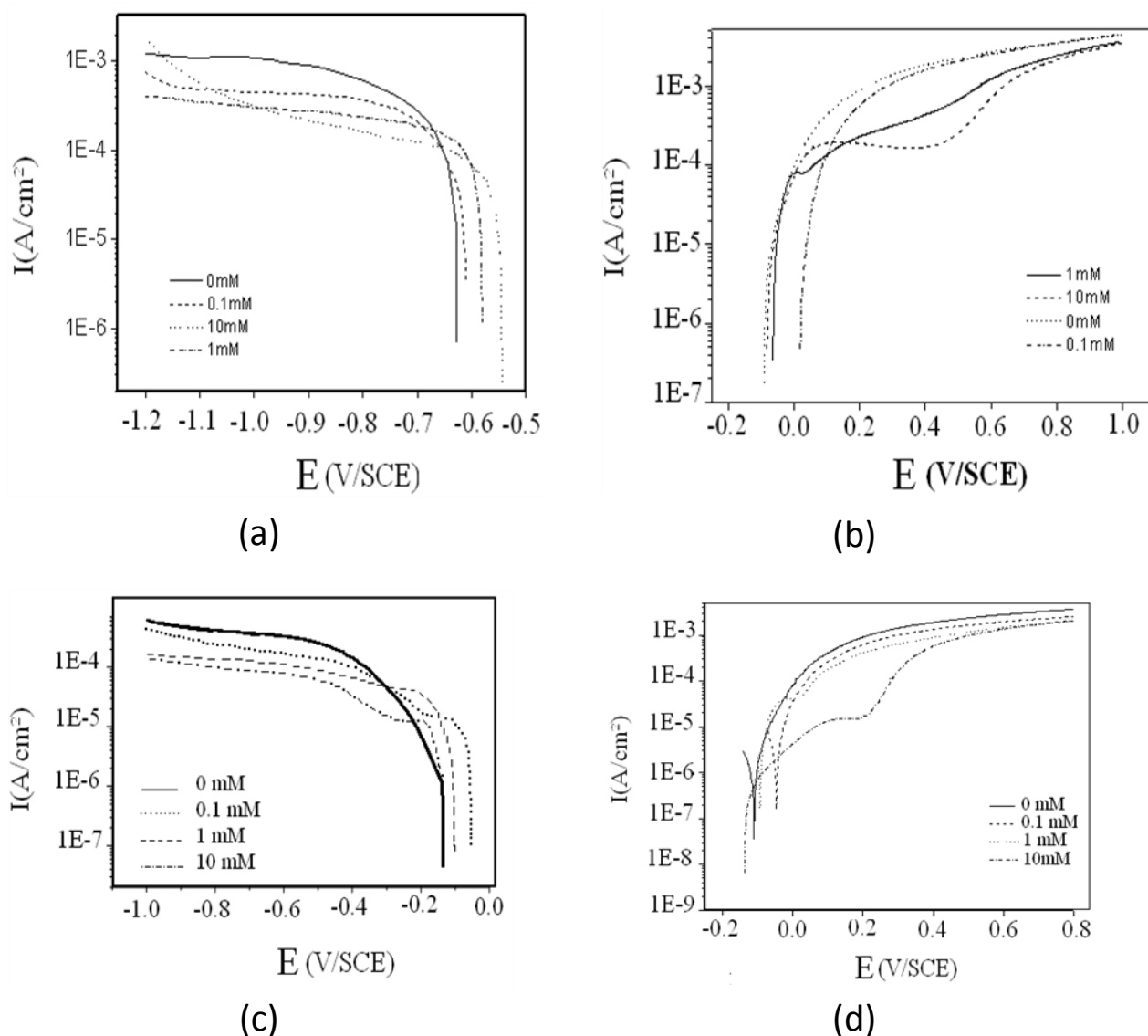


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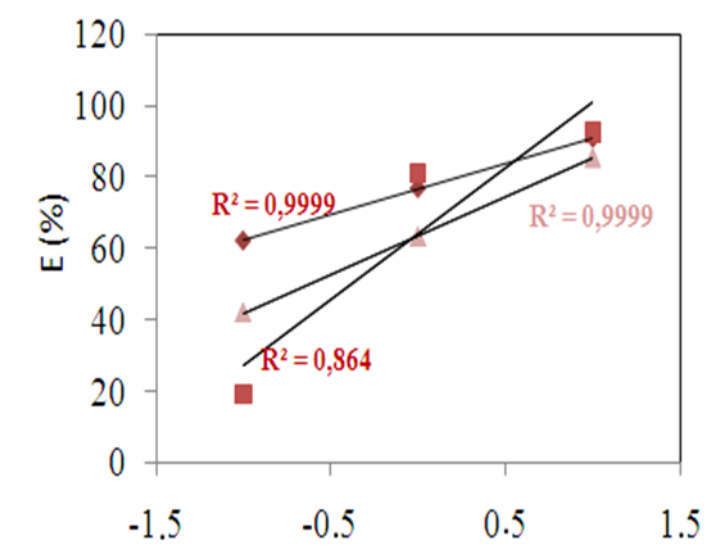


Figure 2 : Variation of inhibitor efficiency vs. the logarithm of ATA concentration

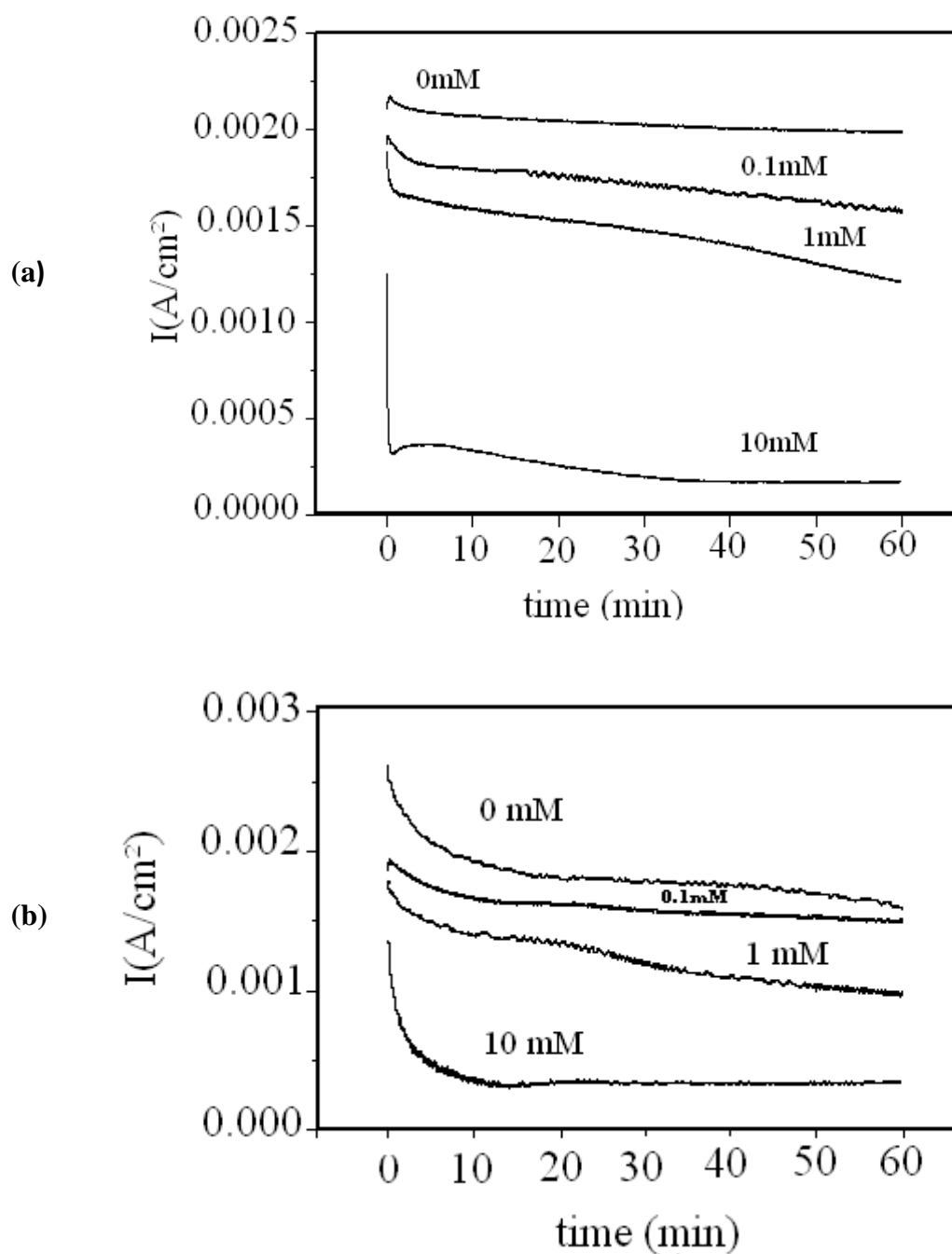


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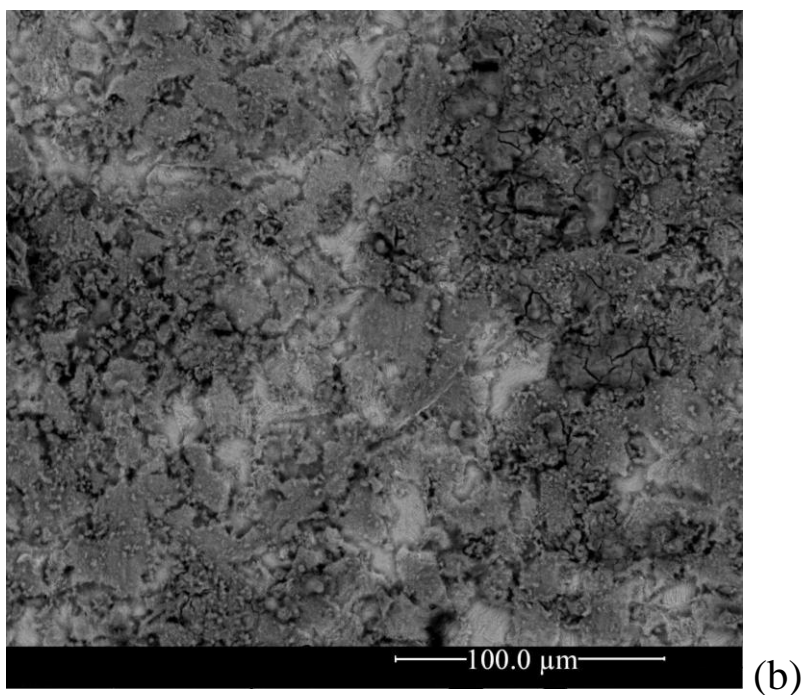
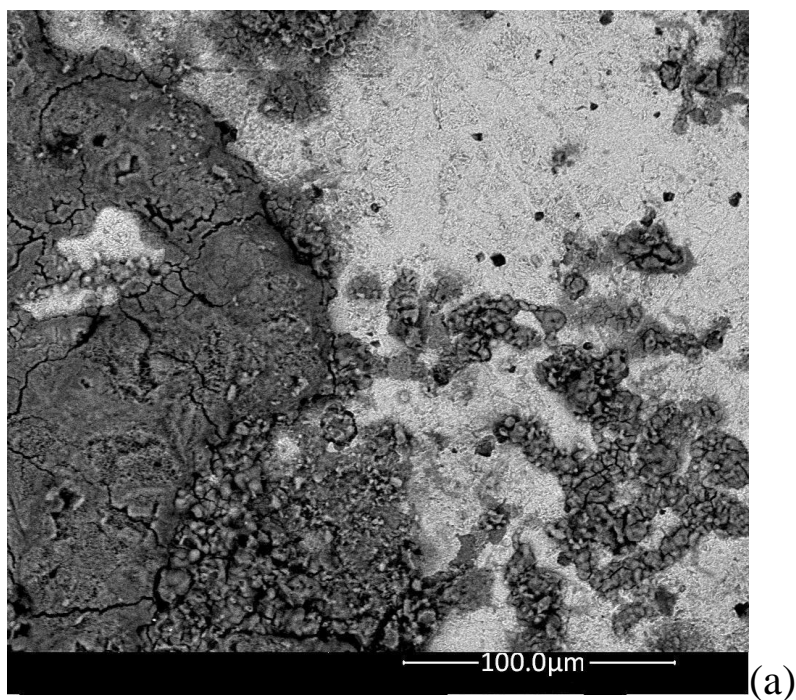


Figure 4: micrograph of the electrode of iron after immersion in urban-marine media without (a) and with 10mM of ATA (b).

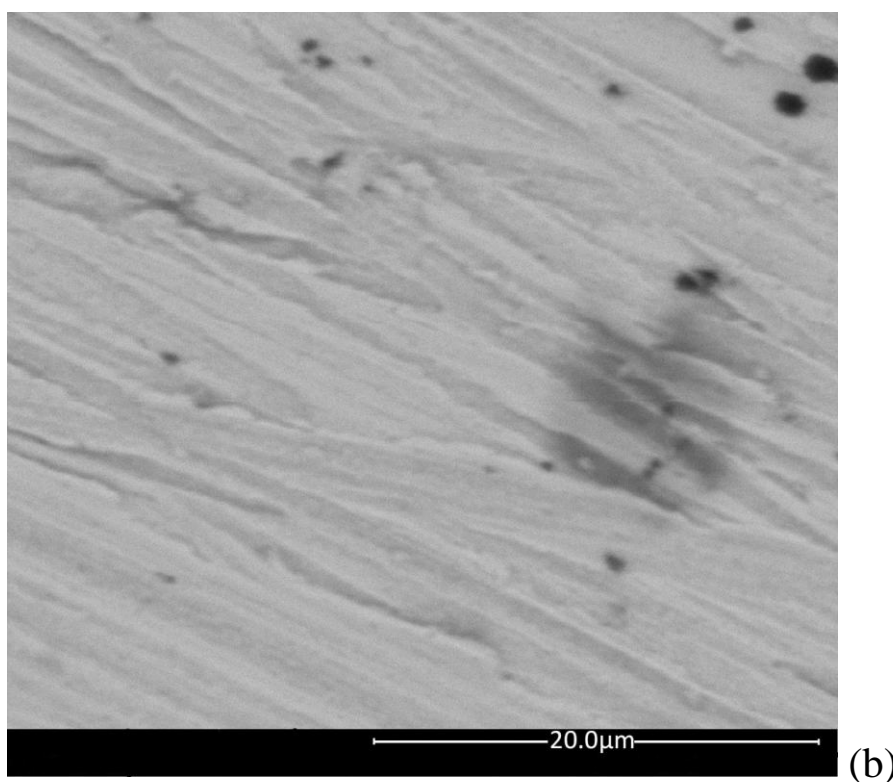
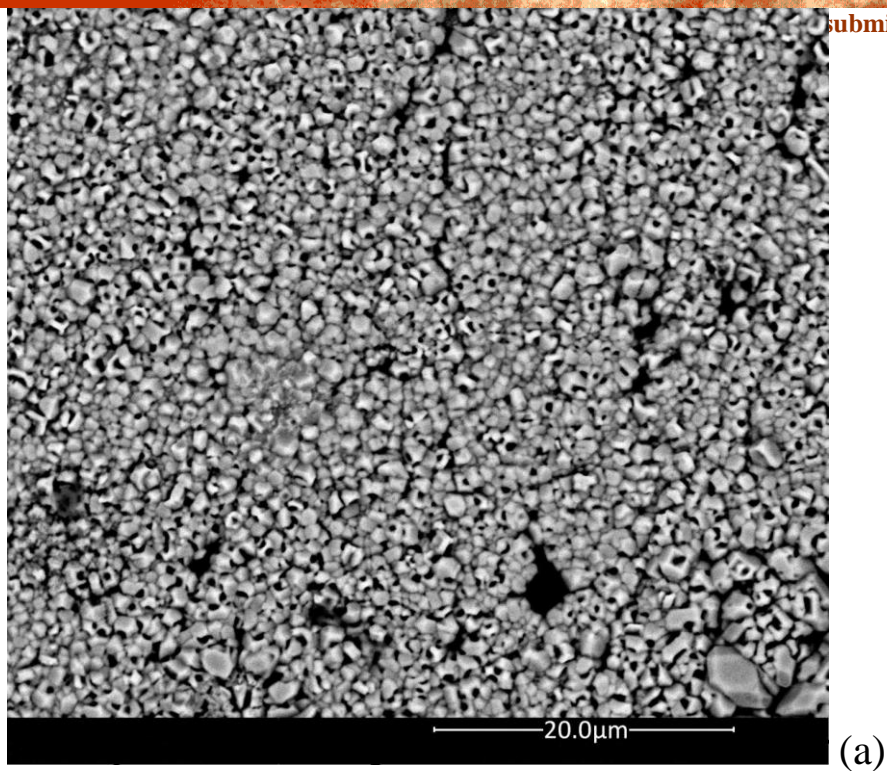


Figure 5: micrograph of the electrode of copper after immersion in urban-marine media without (a) and with 10mM of ATA (b).

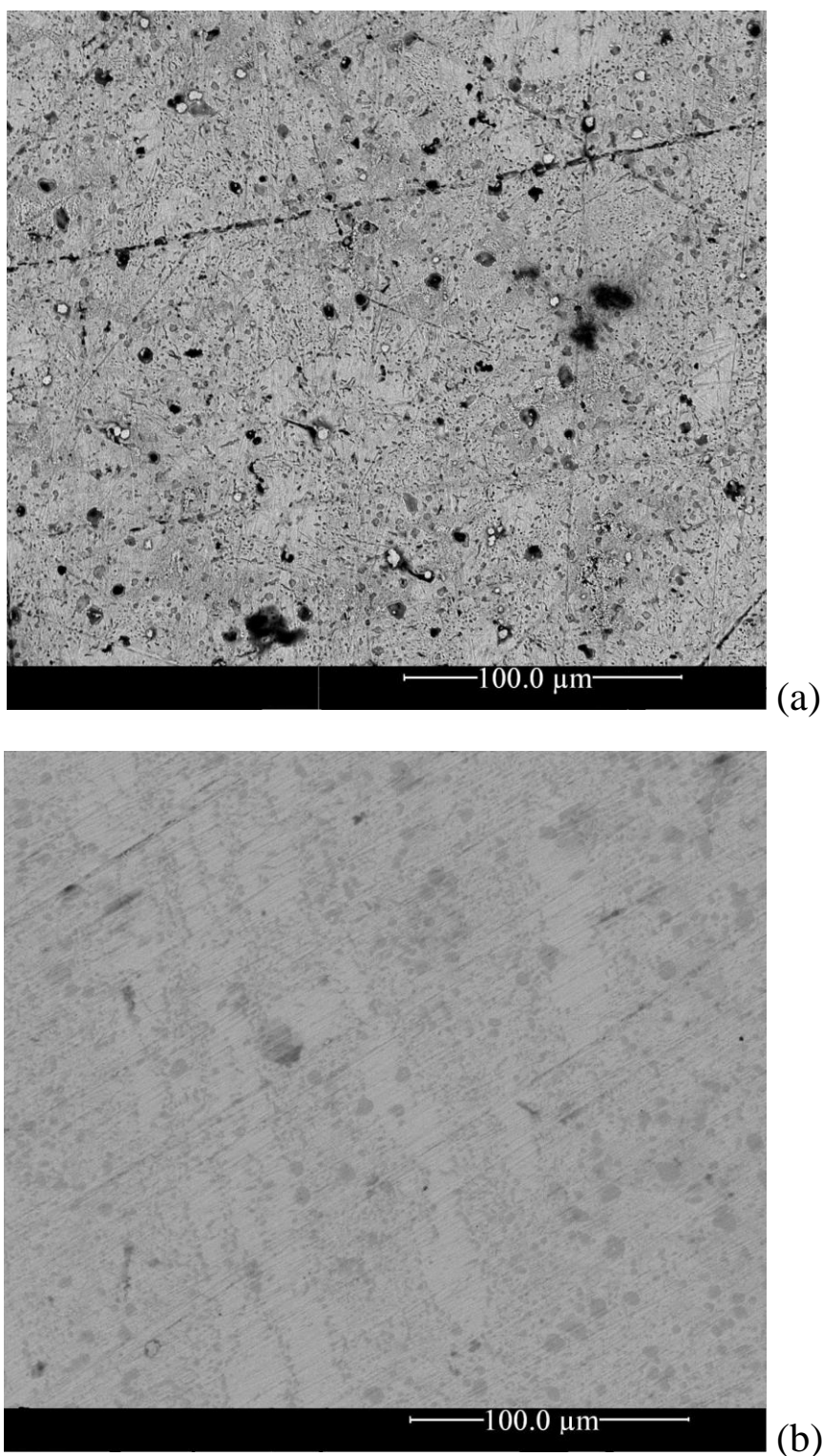


Figure 6: micrograph of the electrode of bronze alloy after immersion in urban-marine media without (a) and with 10mM of ATA (b).

