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CORROSION INHIBITORS FOR BRONZE COVERED WITH SYNTHETIC GOLDEN PATINA

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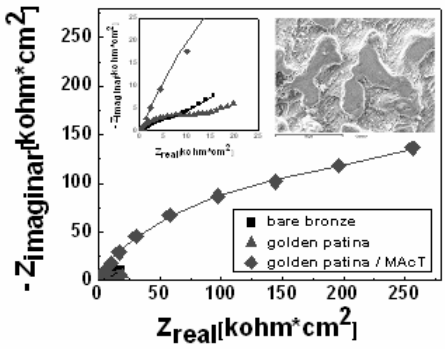
The main objective of this work is tracking the corrosion behavior of a CuSn8 bronze with and without protection, in laboratory conditions. The protection was achieved in several ways, by: (i) applying a golden synthetic patina on bronze surface, (ii) using of two corrosion inhibitors (2-mercapto-5 acetylamino-1,3,4-thiadiazole (MAcT) and benzotriazole (BTA)), and (iii) a combination of the two previous methods. Corrosion tests were carried out in a 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH = 5) solution simulating an acid rain. The protective effect of golden synthetic patina with / without inhibitors was comparatively investigated by electrochemical (polarization measurements, electrochemical impedance spectroscopy) and non - electrochemical methods. The microscopic structure of the bronze surface with / without synthetic patina was investigated through optical microscopy. The chemical composition and the morphology of the corrosion products layer, formed on the bronze / synthetic patina surface in the presence of MAcT were determined by SEM - EDX. The polarization and electrochemical impedance measurements put on evidence that the effectiveness of MAcT as corrosion inhibitor is comparable than that of BTA, which is a remarkable fact, given its non-toxic nature and its accessibility.



INTRODUCTION

Long term conservation of outdoor bronze sculptures involves formation of synthetic patinas on the bronze surface, which additionally confer to artistic objects a pleasant aesthetic aspect.

Synthetic patinas of different colors and compositions are produced by appropriate surface treatments based on chemical[1-4] and electrochemical[1] procedures. The successfulness of synthetic patina formation affects the further behavior of materials in a certain environment. Thus, due to the fact that patinas may be unstable in polluted urban atmosphere, it is important to find solutions which protect bronze covered by patina from further deterioration. For this purpose, various inhibitors are used, such as bezotriazole (BTA),[5] thiadiazoles[5,6] and other organic compounds,[5] especially those containing N and / or S in their molecule. The use of inhibitors is often followed by application of wax or lacquers,[7,8] destined to enhance the stability of the protective layers and the corrosion resistance of bronze objects.

Application of wax sometimes mixed with benzotriazole on patina surface does not satisfy entirely the ethics of restorers. First, the application of wax changes the surface aspect, the prevention layers can undergo cracking and decaying, and second, benzotriazole is known as toxic and also induces a color change of the patina.[9] Therefore, its use has to be avoided and this is why finding new efficient and harmless

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inhibitors for patina preservation remains a challenging subject. On the other hand, although the characterization of patinas is important to understand the corrosion mechanism of bronze in various environments not only for monuments restoration, but also for fundamental studies, only little information on their anticorrosion performance has been reported.[1-4] In this context, the aim of this paper is to investigate comparatively the protective effect of a golden synthetic patina on bronze surface in the absence and in the presence of a non-toxic inhibitor, namely 2-mercapto-5 acetylamino-1,3,4-thiadiazole (MAcT). This inhibitor was used before on bare bronze[10] and on wax-protected patina.[7]

The performance of the inhibitor on the preservation of chemically obtained patina on bronze was compared to that of conventional inhibitor BTA. For this purpose, electrochemical (polarization measurements, electrochemical impedance spectroscopy) and non - electrochemical (SEM – EDX, optical microscopy) methods were used.

RESULTS AND DISCUSSION

1. Potentiodynamic polarization measurements

The experiments started with measuring the potential of the working electrodes in open circuit for 1 hour, in the absence and in the presence of golden synthetic patina / corrosion inhibitors, immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5, adjusted with H_2SO_4). This electrolyte was also used in other works to simulate an acid rain.[11] After reaching the steady-state at open circuit potential (OCP), polarization curves (±200 mV *vs* OCP) were recorded for all studied electrodes in order to determine the corrosion process parameters. The results are shown in Fig. 1 and Table 1. To determine the polarization resistance of the electrodes, polarization curves were recorded, in the potential domain of ± 20 mV *vs*. OCP. The polarization resistance (R_p) values, for each electrode, was calculated with the formula: $R_{p(\Delta E \to 0)} = \frac{\Delta E}{\Delta i}$, are shown in Table 1.

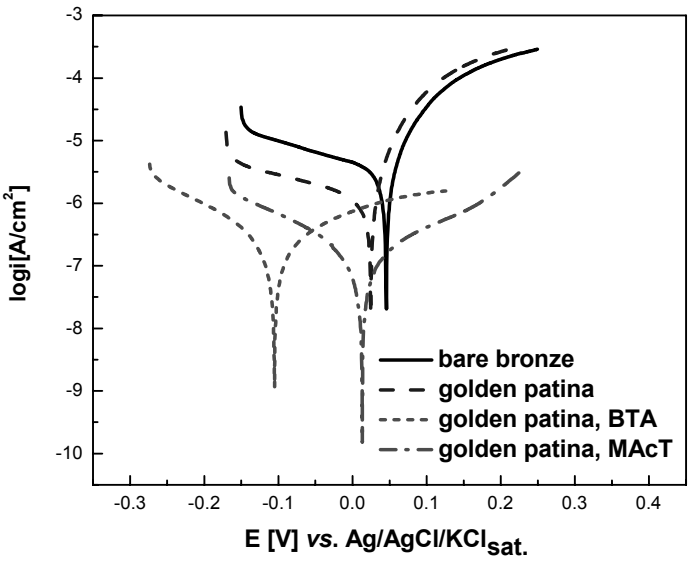


Fig. 1 – The polarization curves (±200 mV *vs* OCP) for the electrodes immersed in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH = 5); scan rate 10 mV / min.

Table 1

Corrosion process parameters for the bronze covered with golden synthetic patina, immersed in 0.2 g / L Na_2SO_4 + 0.2 g / L $NaHCO_3$ (pH = 5) in the presence and absence of corrosion inhibitors

Electrodes	Inhibitors	E_{corr} [mV vs. $Ag/AgCl/KCl_{sat}$]	i_{corr} [$\mu A/cm^2$]	β_a [mV]	$-\beta_c$ [mV]	R_p [$k\Omega cm^2$]	IE [%]
Bare bronze	-	46	5.36	46	284	2.06	-
Golden patina	-	25	1.54	27	188	5.60	71.26
	BTA	-105	0.15	134	110	41.61	95.04
	MAcT	13	0.08	117	110	72.39	97.15

As expected, the lowest corrosion resistance and the highest corrosion current density were noticed in case of bare bronze (R_p = 2.06 kΩcm^2, i_{corr}= 5.36 μA/cm^2, Table 1). In case of the bronze surface covered with golden synthetic patina, the corrosion resistance of bronze increases but the protection efficiency conferred by the patina layer is not spectacular (IE = 71.26 %). The use of BTA led to a clear improvement of the protective properties of the golden patina layer (R_p = 41.61 kΩcm^2) and to a decrease of the corrosion current density (i_{corr} = 0.15 μA/cm^2, Table 1). By comparing these results with those recorded for bronze covered only with synthetic patina layer, it can be concluded that BTA plays a role of barrier against corrosion enhancing the protective effect exerted by the synthetic patina. However, since BTA is a toxic compound, in this work was tested the effectiveness of an innoxious compound, respectively 2 – mercapto 5 – acetylamino 1, 3, 4 – thiadiazole (MAcT) as a corrosion inhibitor for patinated bronze. In this case, the obtained results (R_p = 72.39 kΩcm^2, i_{corr}= 0.08 μA/cm^2) confirmed that the thiadiazole derivative acts as an effective corrosion inhibitor.[8] It should be noted that concomitant use of the golden patina and MAcT as corrosion inhibitor led to the decrease of i_{corr} of about 15 times compared to the bare bronze, proving that MAcT is a better inhibitor than BTA.

2. Electrochemical Impedance Spectroscopy

Impedance spectra were recorded and the results obtained for the bronze covered with golden synthetic patina in the presence of corrosion inhibitors were compared with the results obtained in case of bare bronze. In all cases, the corrosion behaviour was studied by recording the impedance spectra after 1 hour, 48 hours and respectively 72 hours of immersion in the corrosive solution (0.2 g/L $NaSO_4$ + 0.2 g/L $NaHCO_3$, pH = 5). Based on the results that are shown in Fig. 2, it can be noticed that the impedance spectra exhibit a capacitive behaviour in the whole frequency domain.

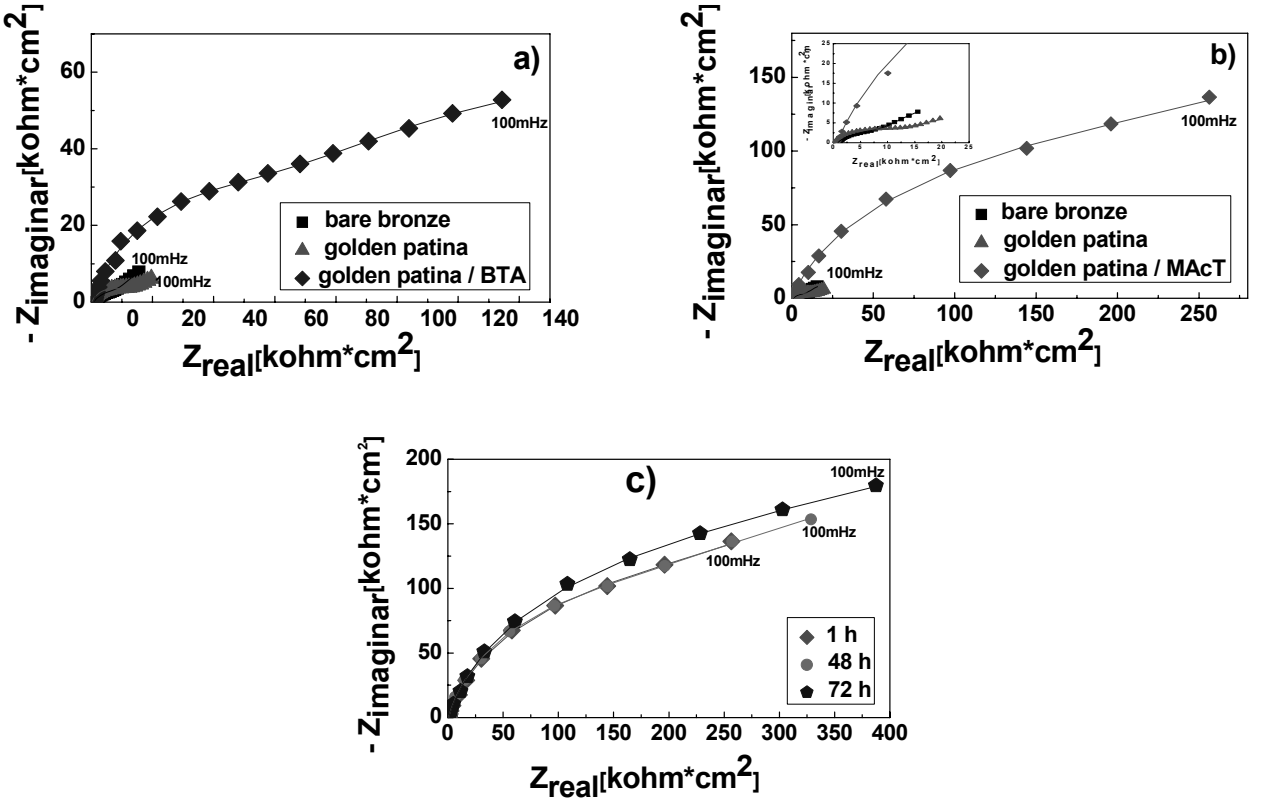


Fig. 2 – Nyquist impedance diagrams of the bronze electrodes in Na_2SO_4 / $NaHCO_3$ (pH 5) solution; influence of inhibitors after 1 h of immersion (a, b) and of immersion time for golden synthetic patina in the presence of MAcT (c); the lines represent fitted data.

The experimental impedance spectra were analyzed for the bare bronze electrode by fitting to a 2RQ equivalent electrical circuit (Fig. 3a) and for the electrodes covered with golden patina / inhibitors by fitting to a 3RQ equivalent electrical circuit (Fig. 3b), which was previously used to model bronze corrosion in the presence of corrosion inhibitors and artificial patinas.[10,12-14] The equivalent electrical circuit from Fig. 3a consists of: the R_{ct} - C_d couple at high frequencies, representing the charge transfer resistance R_{ct} and the double layer capacity, C_d at the bronze electrodes | electrolyte interface and a second couple (R_F – C_F) at low frequencies, where R_F represent the faradic resistance of the corrosion products accumulated at the interface and C_F, the faradic capacity due to an oxidation - reduction process taking place at the electrode surface, probably involving the corrosion products. R_e represents the electrolyte resistance. The 3RQ circuit contains an additional R_f and C_f couple, where R_f is the resistance representing the ionic leakage through pores of the oxide film and C_f is capacitance due to the dielectric nature of the patina / inhibitor film. Coefficients n_f, n_d and n_F: represent the depressed feature of the capacitive loop in *Nyquist* diagram ($0 < n \leq 1$). The values of C_F C_d and C_f were calculated using the equation $C = (R^{1-n}Q)^{1/n}$, where Q is the constant phase element.

The parameters obtained by fitting the equivalent electrical circuits for bare bronze and bronze covered with golden synthetic patina are shown in Table 2. The quality of fitting procedure was evaluated by the chi squared (χ^2) values, which were of order 10^{-4} -10^{-3}.

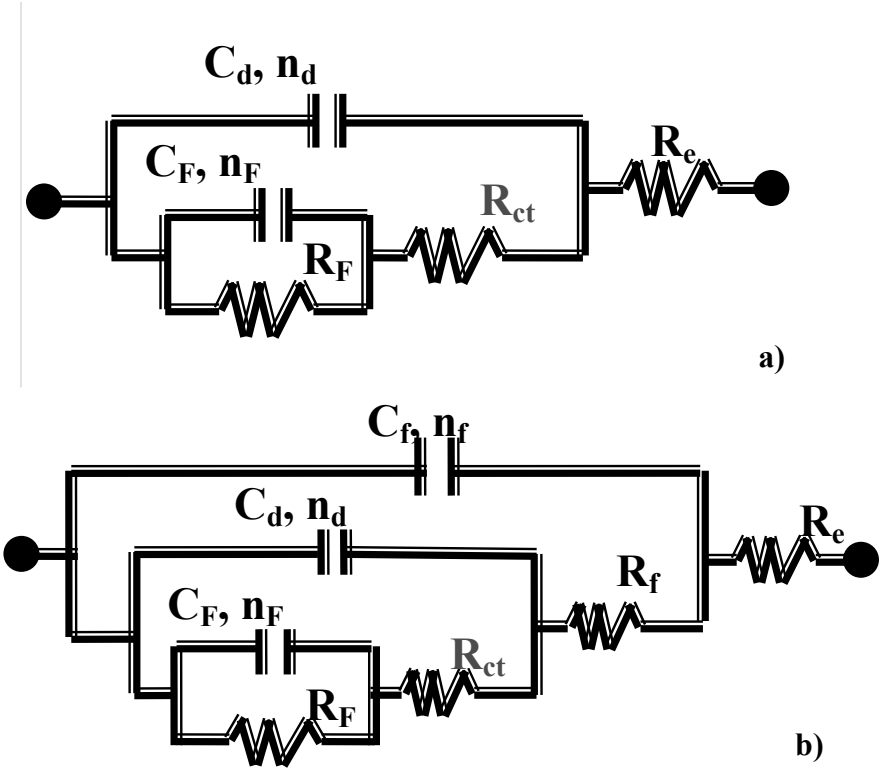


Fig. 3 – The equivalent electrical circuits used for fitting of the experimental results: a) 2RQ, b) 3RQ.

Table 2

Electrochemical parameters of bronze corrosion in Na_2SO_4 / $NaHCO_3$ (pH 5) solution obtained in the absence / the presence of golden synthetic patina and of corrosion inhibitors

Sample	Time [h]	R_e [kΩcm^2]	R_f [kΩcm^2]	C_f [μF/cm^2]	R_t [kΩcm^2]	C_d [μF/cm^2]	R_F [kΩcm^2]	C_F [μF/cm^2]	R_p^* [kΩcm^2]	IE[%]
Bare bronze	1	0.512	-	-	0.74	7.31	19.07	499	19.81	-
	48	0.322	-	-	5.09	9.74	16.76	405	21.85	-
	72	0.291	-	-	3.58	5.49	10.54	402	14.12	-

Table 2 (continued)

Golden patina	1	0.146	0.483	0.258	13.46	18.07	6.715	327	20.66	4.11
	48	0.195	0.544	0.267	14.52	32.69	9.892	238.9	24.96	12.45
	72	0.170	0.509	0.266	14.30	34.43	8.741	252.3	23.55	40.04
Golden patina / BTA	1	0.387	28.33	0.656	3.91	0.534	164.8	0.978	197.04	89.94
	48	0.378	24.24	0.635	8.22	1.359	149.4	0.194	181.86	87.98
	72	0.374	51.34	0.542	8.37	0.207	528	0.429	587.71	97.59
Golden patina / MAcT	1	0.354	68.75	0.137	93.83	0.652	209	0.252	371.58	94.66
	48	0.360	73.28	0.147	342.39	6.816	205.22	0.083	620.89	96.48
	72	0.373	52.98	0.109	288.71	1.963	306.37	0.148	648.06	97.82

* $R_p=R_f + R_{ct} + R_F$

For a redox process at the electrode surface, the value of the polarization resistance ($R_p = R_f + R_{ct} + R_F$) can be correlated with the corrosion rate. Thus, analysing the data from Table 2, it can be observed that, in case of bare bronze, the value of the corrosion resistance increases after 48 hours, but not significantly, due to the formation of the oxide film which inhibits the corrosion process on the surface of bare bronze. However, after 72 hours the value of the corrosion resistance decreases, which can be explained by the fact that, the oxide layer formed is unstable and is destroyed over time. Thus, the process of degradation continues.

In case of the bronze covered with golden patina, one can see that the values of the corrosion resistance are not suffering significant changes in time (Table 2). This behaviour can be explained by the fact that the golden synthetic patina is relatively stable in time. In the presence of the corrosion inhibitors we can see that, in both cases, the values of corrosion resistance increase compared with bare bronze / golden patina, thus confirming the results obtained from the polarization curves. It should be noticed that in combination with golden patina, MAcT seems to be a better inhibitor than BTA, exhibiting increased polarization resistances and larger inhibiting efficiencies. These results are in agreement with the polarization measurements.

As shown in Fig. 2 and Table 2, the protective properties of inhibitors increase in time. The highest protection is observed in the case of golden patina / inhibitor combinations, which is in accordance with the low values of C_d.[15]

3. Optical microscopy

In order to confirm the electrochemical results, the surface of corroded bronze electrodes, after 1 hour immersion time and after the polarisation measurements, was first analysed by optical microscopy.

The optical microscopic analysis (Fig. 4 a) showed that, in case of bare bronze the corrosion product layer is not uniform and, moreover, one can see the pits appearance, proving that the bare bronze was severely corroded. On the contrary, it can be seen that, after the corrosion tests, the corrosion products layer formed on bronze covered with golden patina in presence of MAcT is relatively uniform and that no locally corroded areas are visible (Fig. 4b). In what the surface of bronze covered with golden patina / BTA is concerned, the corrosion products layer is also uniform (Fig. 4c), but the colour of the golden synthetic patina changed and became greenish-black. It should be noticed that the patina layer remained adherent on the bronze surface after the corrosion tests in both cases when inhibitors were used.

4. Morphological characterization of the corrosion products by SEM – EDX

More detailed information about the composition of the corrosion products layer was obtained by SEM-EDX analysis carried out on the corroded bronze electrodes covered with golden synthetic patina in the presence of MAcT. Thus, SEM-EDX analysis was performed at different points of the electrode's surface and some results are presented in Fig. 5 and Table 3. The results were compared with those on bare bronze and bronze covered only with golden patina reported previously.[8]

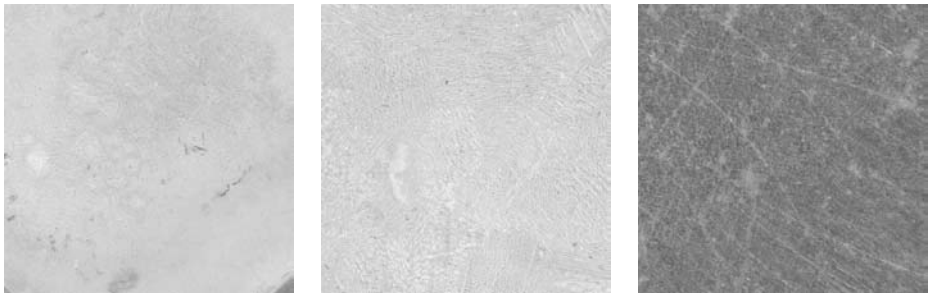
Analysing the results from Table 3 and Fig. 5, it can be observed a relatively uniform distribution of the elements that form the golden synthetic patina

layer in the presence of MAcT. The EDX analysis at different points indicated the presence of copper, oxygen, carbon, sulfur, and tin, whereas aluminum, silicon, phosphorus, chlorine, zinc and lead were present as minor elements. The silicon presence can be explained by its participation to the casting process of molten bronze. The presence of S was attributed both to $CuSO_4$ used for patina synthesis and to the inhibitor (MAcT) adsorbed at the interface on the golden synthetic patina.

Based on the X-ray maps (Fig. 7) for O and Sn it can be assumed that in the golden patina layer / MAcT, tin oxide was formed on almost the entire surface of the bronze electrode. The formation of the Sn-based compounds stabilized the artificial patina, which explains the high corrosion resistance of bronze CuSn8.[16]

From the distribution of elements S and Pb, four areas rich in these elements can be observed in the lower part of the maps. This may be due to the existence of lead sulphide. From the X-ray maps for O and Si it can be assumed that in the golden patina layer SiO_2 was formed in small quantities.

Based on SEM / EDX analysis it can be concluded that the thin, continuous, adherent and relatively homogenous corrosion products layer formed in the presence of golden patina / MAcT is responsible for the better corrosion resistance of the bronze samples.



a) b) c)

Fig. 4 – Microscopic observation of corrosion products formed on bare bronze surface (a), golden patina / MAcT surface (b), golden patina / BTA surface (c), respectively, after corrosion tests: 80X.

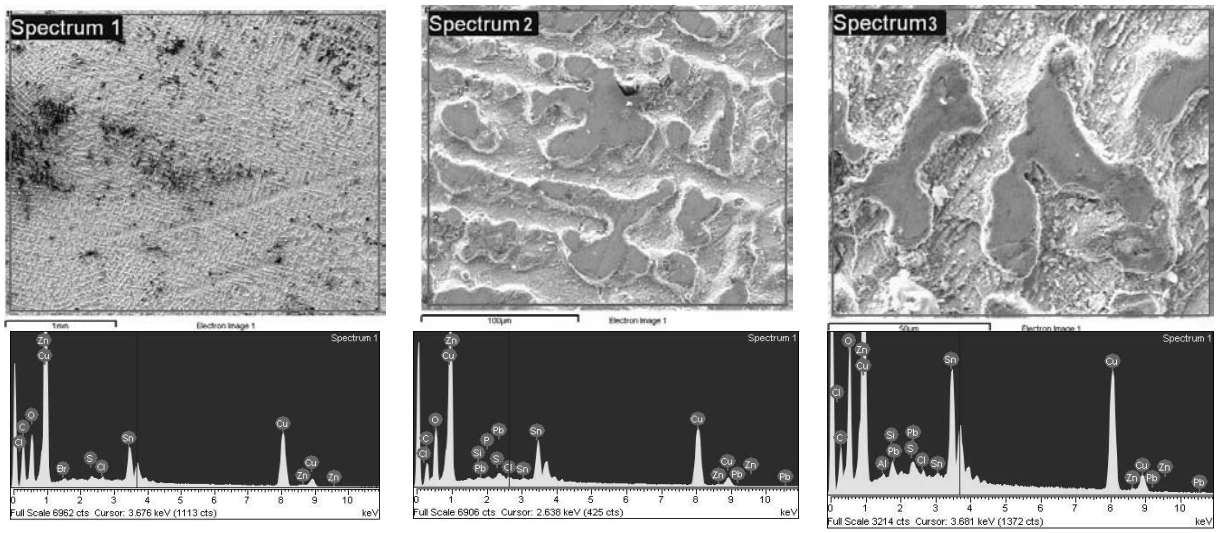


Fig. 5 – SEM / EDX results obtained on the surface of bronze electrode covered with golden artificial patina / MAcT, after corrosion tests.

Table 3

Elemental composition [%] of the corrosion products formed at three different points on the bronze electrode surface covered with golden synthetic patina / MAcT, determined by EDX analysis

	C	O	Al	Si	P	S	Cl	Cu	Zn	Sn	Br	Pb
1	21.25	13.27	-	-	-	0.30	0.34	48.76	2.16	13.31	0.61	-
2	11.26	14.61	-	0.22	0.27	0.23	0.32	53.77	2.03	16.14	-	1.15
3	9.07	17.20	0.21	0.71	-	0.36	0.31	49.23	2.16	19.47	-	1.27

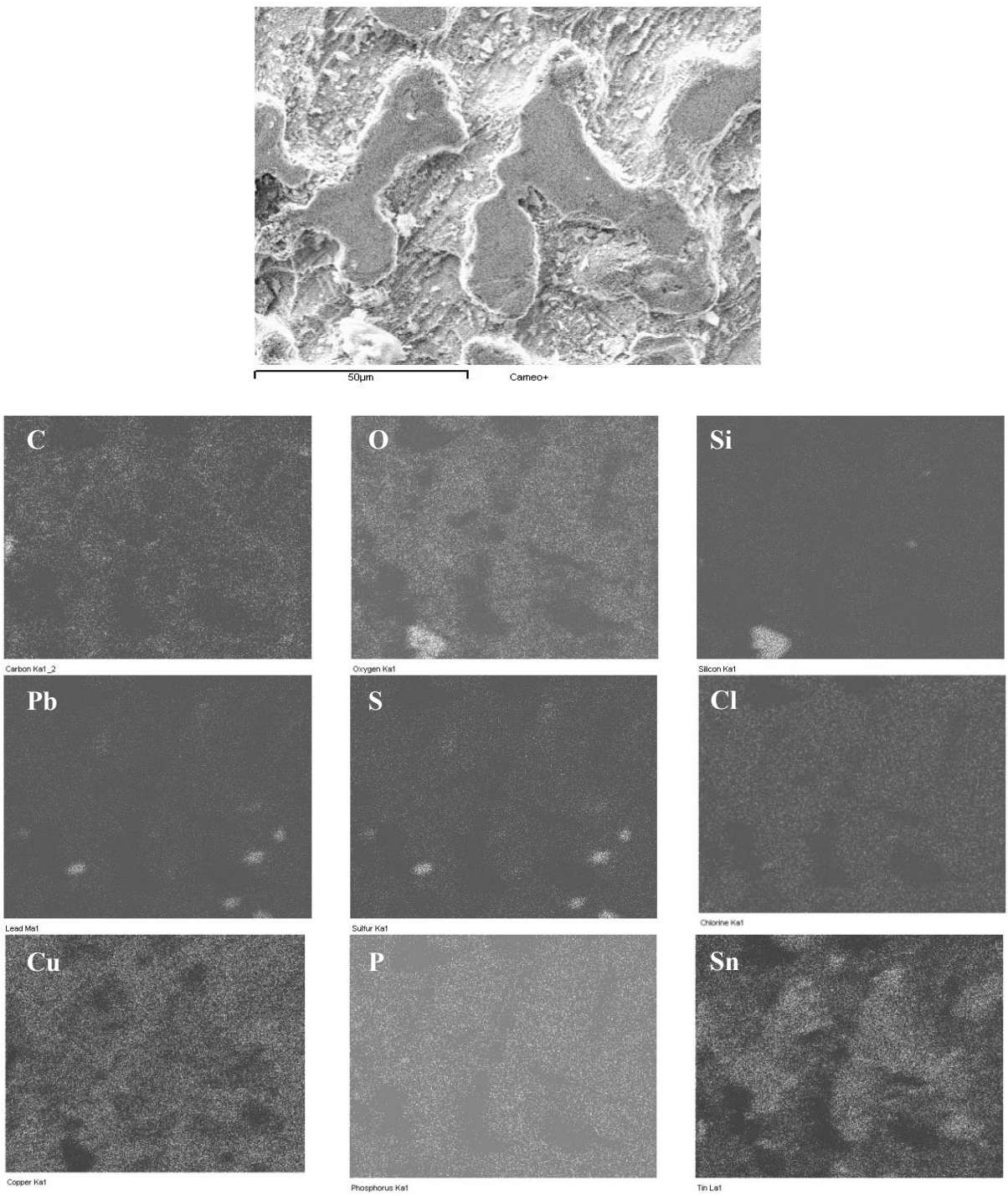
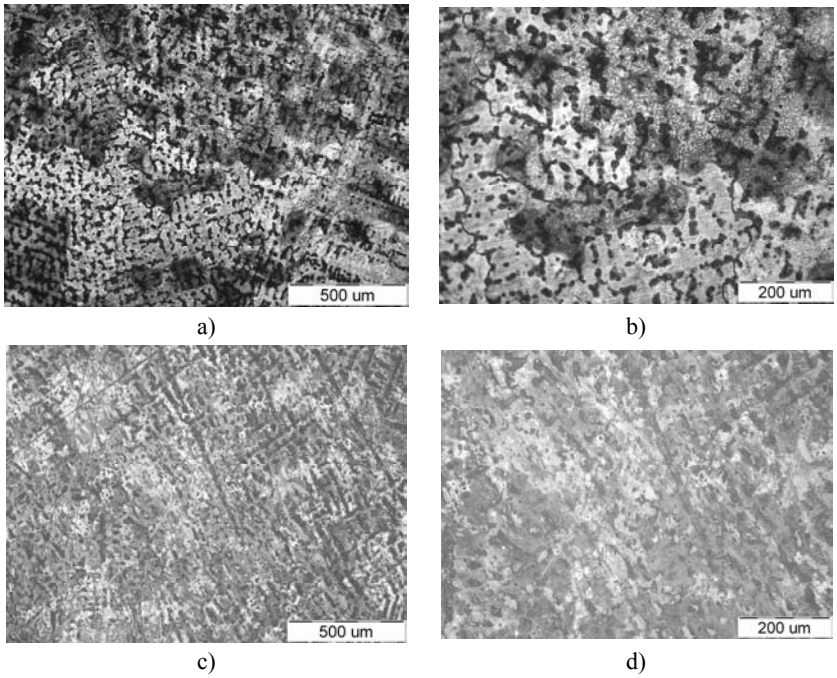


Fig. 6 – Mapping results obtained on surface of bronze electrode covered with golden patina /MAcT. X - ray maps for C, O, Pb, S, Si, Cu, P, Sn.



a) b)

c) d)

Fig. 7 – Microscopic structure of bronze used for electrochemical studies: bare bronze a), b); bronze covered with golden synthetic patina c), d) at magnification x100 respectively x200.

EXPERIMENTAL

The working electrodes, made of bronze ingot (CuSn8) (the composition was reported in another paper[7]), were cast in a gypsum mold in the form of a bar, at the foundry of University of Art and Design, Cluj-Napoca, Roumania. Fig. 7 presents the microscopic structures of electrodes, magnified at 100X and 200X, which were subjected to accelerated corrosion in an environment that simulated acid rain. The images in Fig. 7a,b display the dendritic segregation of the α solid solution and interdendritic segregations of eutectoid α + δ in small quantities, previously reported in.[7] The optical micrograph images of the artificially patinated bronze (Fig. 7c,d) show a discontinuous layer of corrosion products (artificial patina) reproducing the dendritic microstructure of the substrate.

The samples with an area of 2 cm^2 and the diameter of 15 mm were placed in a PVC tube, while the sealing was assured with epoxy resin (Table 4); for electrical contact a metal rod was attached.

Artificial patina was prepared by chemical methods on the polished bronze surface in several steps, using the substances mentioned in Table 4. The stages of the patination process were: (i) wet polishing of the bronze surface, using aluminum oxide; (ii) degreasing in acetone; (iii) maintaining the bronze samples in solution for 7 – 15 min., at a given temperature (30 °C) until the patina layer is formed; (iv) washing with distilled water until neutral; (v) drying with ethyl alcohol.

The inhibitor used in the experiments was a non-toxic thiadiazole derivative, respectively 2-mercapto-5 acetylamino-1,3,4-thiadiazole ($C_3H_5N_3OS_2$, MAcT) from Sigma Aldrich and the obtained results were compared with those recorded with benzotriazole ($C_6H_5N_3$, BTA, Sigma Aldrich). Each of these compounds was dissolved in the corrosive solution consisting of 0.2 g/L Na_2SO_4 and 0.2 g/L $NaHCO_3$ (pH = 5) in a concentration of 1mM. Previous studies[6] have shown that this is the optimal concentration for the examined system.

The inhibiting efficiencies (IE) conferred by the golden synthetic patina in the absence / presence of corrosion inhibitors were determined using the formula:

$$IE[\%] = \frac{R_p - R_p^0}{R_p} x100 \quad (2)$$

where: R^0_p and R_p are the values of the polarization resistance for bare bronze and for bronze covered with golden synthetic patina / inhibitor, respectively.

Table 4

Substances used to create artificial patina

	Chemical composition of the solution	Chemical formula	Concentration [g/L]	Duration of immersion / temperature
	Sodium hydroxide	NaOH	50	7-15 minutes / 30 ºC
	Oxalic acid	$C_2H_2O_4$	30	
	Copper sulphate	$CuSO_4$	50	

The electrochemical corrosion measurements were performed on a PC – controlled electrochemical analyzer AUTOLAB - PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode (bronze), an $Ag/AgCl/KCl_{sat}$ electrode as reference electrode and a platinum counter electrode. Anodic and cathodic polarization curves were recorded in a potential range of ± 20 mV and of ± 200 mV *vs.* the value of the open circuit potential, with a scan rate of 10 mV / min, after 1 hour immersion in corrosive solution.

The electrochemical impedance spectroscopy measurements (EIS) were recorded at the open circuit potential value after 1 hour immersion of the bronze electrode in the corrosive solution. The impedance spectra were recorded after 1, 48 and 72 hours in the frequency range 10 kHz - 100 mHz with an AC voltage amplitude of 10 mV (30 points / Hz decade).

For the microscopic study (by optical microscopy OLIMPUS GS 51), the electrodes surfaces was polished on the sample polishing machine with alumina paste, after which the surface was attacked with ammoniacal cupric chloride. The studies of the samples surface after corrosion tests were analyzed using optical microscope (Nikon SZM 1000) at a magnification of 80X. The bronze surface covered with golden patina in the presence of MAcT, was analyzed morphological by SEM using a Jeol JEM5510LV (Japan) microscope coupled with an Oxford Instruments EDX Analysis System, INCA 300 (UK) at 15kV and spot size 39 μm.

CONCLUSIONS

The corrosion properties of bronze covered with golden synthetic patina in the presence of corrosion inhibitors (BTA and MAcT) were investigated in a solution of Na_2SO_4 and $NaHCO_3$ (acidified to pH = 5 by adding H_2SO_4) which simulated an acid rain. The golden synthetic patina was applied by a chemical method. The best protection efficiency was exerted by golden artificial patina in the presence of MAcT (around 97%). This fact is also confirmed by the electrochemical impedance spectroscopy measurements. It should be noted that the effectiveness of MAcT is comparable that of BTA, which is a remarkable fact taking into consideration its non-toxic nature and its accessibility. Moreover, its use does not affect the color of the golden patina.

Based on SEM / EDX analysis it can be concluded that in the presence of the synthetic golden patina and of MAcT, the corrosion products layer formed is thin, relatively continuous, adherent and chemically homogenous and is mainly composed of tin compounds, that improve the corrosion resistance.

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