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ELECTROCHEMICAL CHARACTERISTICS OF ELECTROCHEMICALLY PATINATED BRONZE

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Abstract

In this study patina was formed on bronze substrate by electrochemical technique. The linear polarization curves and electrochemical impedance spectroscopy (EIS) have been employed to study the corrosion performance of the patined bronze sample in simulated acid rain at the beginning of long-term immersion; with the increase of immersion time. However, the corrosion resistance of the patined bronze sample was deteriorating after 1 day of immersion. Moreover, the large areas of the patining have fallen off the substrate after 30 days of immersion.

Keywords: bronze substrate, patina, simulated acid rain, SEM, EIS

1. Introduction

Actual researches are conducted on the effects of pollutants from the exterior environment on different materials or on their effects on human health. But the presence of these agents in outdoor atmosphere, museums, libraries, archives etc. is a permanent threatening to the cultural heritage items, due the complex chemical processes, mainly oxidation reactions, which irreversibly affects the constituent materials structure [1].

Bronze is an alloy with a wide application both contemporary and historic. Since bronze has good resistance against atmospheric corrosion, it is an alloy frequently employed in works of art (sculptures, monuments, bells, etc.) and in bronze ornaments for building constructions. When exposed to atmospheres contaminated with chlorides, copper from bronze alloys forms a layer of corrosion products usually of brown-green or green-blue colour which is known as ‘patina’ [2]. Patina is the result of the chemical interaction between traces contaminant elements from atmosphere, mainly sulphates and chlorides, and cooper materials.

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The copper weathering chemistry and associated mechanisms have been quite well studied. Nassau et al. have identified on Cu patinas formed in the atmosphere the following main compounds: cuprite, Cu_2O, brochantite, $Cu_4SO_4(OH)_6$, antlerite, $Cu_3SO_4(OH)_4$, ponsjankite, $Cu_4SO_4(OH)_6{\cdot}H_2O$, atacamite, $Cu_2Cl(OH)_3$ [2-4].

In the present work it was studied the electrochemical corrosion behaviour of patina formed on bronze substrate by electrochemical technique in simulated acid rain. The EIS technique was used to detect the pores and pinholes in the patinated sample and asses their effect on the corrosion resistance behaviour over longer immersion time.

2. Experimental

2.1. Sample preparation and characterization

The substrate material used in this study was a bronze sample: 81Cu 19Sn (%wt.), which was cut to 0.28 cm^2. The sample was taken from a fissured church bell with an age of about 150 years old.

The substrate was ground with SiC abrasive paper up to 2000 grit, and polished with 1 μm alumina suspension to obtain a mirror-like surface. The sample was degreased with ethyl alcohol followed by ultrasonic cleaning. The electrochemically patining was realized with a natural sulphurous water (Nicolina-Iasi). The electrochemical reaction was conducted into an electrochemical cell with three electrodes: the bronze substrate was anode, a platinum electrode was cathode and the reference electrode was a saturated calomel electrode (SCE). All potentials referred to in this article are with respect to SCE. The anodic patina formation was carried out with a VoltaLab 21 potentiostat (PGP 201 type – Radiometer Copenhagen). A potential of +300 mV was applied for 5 minutes. After washing, the sample was dried under a hot air stream.

The planar morphologies of the patinated sample was studied by Vega Tescan scanning electron microscope (model VEGA II LMH) having detector (model xflash, Bruker) for EDX analysis.

2.2. Electrochemical measurements

Electrochemical corrosion resistance was studied in simulated acid rain. The chemical composition of the simulated acid rain was detailed in a previous paper [5]. A copper sheet was attached onto the unpatinated side of the specimen, which was mounted by epoxy-resin with 0.28 cm^2 monitoring patinated area. The experimental set-up consisted of a conventional three electrode cell containing the working electrode, a saturated calomel electrode (SCE) and a platinum sheet as a counter electrode.

The zero current potential (ZCP) and the corrosion current density (i_{corr}) for unpatinated and patinated samples was determined from plots of the linear polarization curves at ± 150 mV vs. open circuit potential after 1 hour immersion in simulated acid rain, at 20°C, using an VoltaLab 21 potentiostat. The scanning rate was 1 mV/s.

Electrochemical impedance spectroscopy (EIS) measurements were carried out by a VoltaLab 40 potentiostat (PGZ 301 type – Radiometer Copenhagen) controlled by a personal computer with dedicate software (VoltaMaster 4), after different immersion periods. The alternating current (AC) impedance spectra were obtained, with a scan frequency range of 10 kHz to 10 mHz with amplitude of 10 mV. The EIS data were registered at open circuit potential at different immersion time in simulated acid rain, at 20°C. In order to supply quantitative support for discussions of these experimental EIS results, an appropriate model (Convertor-Radiometer, France and ZSimpWin-PAR, USA) for equivalent circuit (EC) quantification has also been used. In this study a constant phase elements (CPE) was used in the fitting procedure to obtain good agreement between the simulated and experimental data instead of an ideal capacitor. The impedance of the CPE is given by [6]:

$$Q = Z_{CPE} = \frac{1}{C(j\omega)^n} \tag{1}$$

where for n = 1, the Q element reduces to a capacitor with a capacitance C and, for n = 0, to a simple resistor. The n is related to a slope of the log Zmod vs. log frequency Bode–plots, ω is the angular frequency and j is imaginary number ($j^2 = -1$).

3. Results and discussion

3.1. Patining characterization

The planar SEM images of the bronze electrochemically patinated are shown in Figure 1. There are many micro-particles on the surfaces of the film, as can see from Figure 1a. The surface of bronze patinated revealed a porous structure at high magnification (Figure 1b).

Local compositional analysis (Figure 2) of the electrodeposition products indicated that they were patina. The EDX spectrum after electrochemical deposition, attest the presence of S, Cl and O on bronze patinated surface.

3.2. Electrochemical tests

Standard techniques were used to extract ‘zero current potential’ (ZCP) and corrosion current density (i_{corr}) values from the potentiodynamic polarization plots. The average values of ZCP and i_{corr} were determined from linear polarization curves by using the VoltaMaster 4 program, defining the ZCP as the voltage at which the current reaches a minimum during the forward potentiodynamic polarization scan.

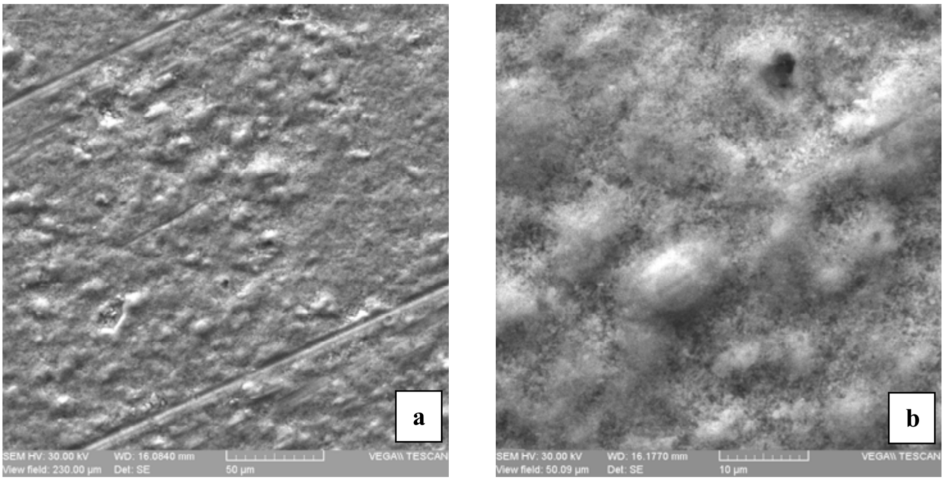

Figure 1. SEM micrographs of the electrochemically patina formation on bronze substrate.

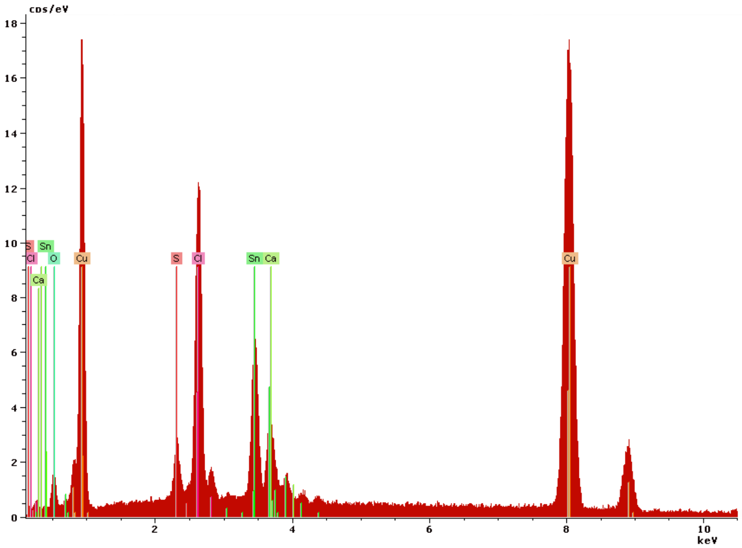

Figure 2. EDX spectrum for the electrochemically patinated bronze surface.

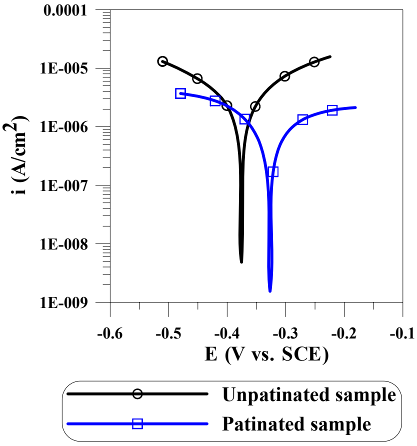

Figure 3. Potentiodynamic polarization curves for unpatinated and patinated bronze samples after 1 hour immersion in simulated acid rain; 1 mV/s and 20° C.

The corrosion current density (i_{corr}) is representative for the degradation degree of the alloy. Figure 3 and Table 1 show the results of the electrochemical polarization measurements recorded in a range of ± 150 mV vs. open circuit potential (E_{OC}) on unpatinated and patinated bronze samples, after 1 hour immersion in simulated acid rain. It is evident from Figure 3 that there is a decrease of the anodic current of the patinated bronze sample with respect to the unpatinated bronze sample. This demonstrates that the patinated sample has a better corrosion resistance than that of the substrate (unpatinated sample), and this results in smaller values for the corrosion current densities. The corrosion current density for unpatinated specimen are approximately four times higher than in the case of patinated bronze sample obtained in the same conditions.

Table 1. The corrosion parameters of the unpatinated and patinated bronze samples in simulated acid rain.

Sample	**ZCP (mV)**	**i_{corr} (μA/cm^2)**
Unpatinated bronze	-375	2.5
Patinated bronze	-325	0.6

From this electrochemical DC determination, it is not possible to distinguish unambiguously a different corrosion resistance for the patina electroformation in this environment, as only slightly corrosion current density values could be related to the sample patining (Table 1).

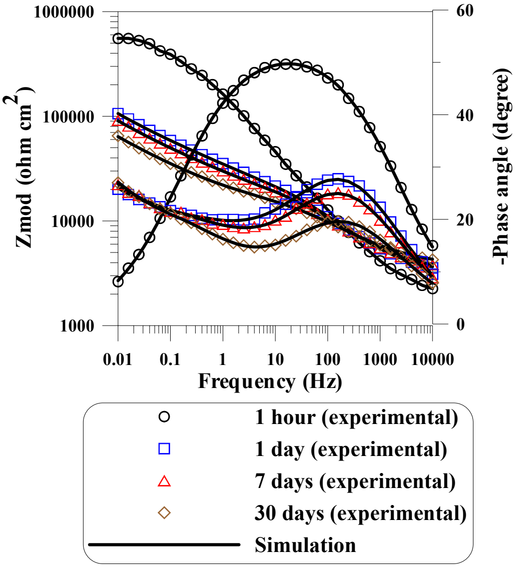

Figure 4. Bode plots for electrochemically patinated bronze recorded at open circuit potential, after different time of immersion in simulated acid rain.

Electrochemical Impedance Spectroscopy (EIS) has been employed to detect the pores and pinholes during the patina forming and to asses their effect on the corrosion behaviour over longer immersion time. The EIS spectra are shown in Bode plots of the logarithm of the impedance magnitude and of the phase angle as function of the frequency logarithm. In the Bode plot, impedance at high frequency represents the response of the coating, exhibiting thus the patining information, while at the low frequency; the information about the process is related to the reaction at the substrate/solution interface.

Bode plots of the bronze electrochemically patined immersed for different periods in simulated acid rain are shown in Figure 4. The phase angle plots reveal only one peak for patina formating after 1 hour immersion in simulated acid rain, indicating the involvement of a single time constant. In fact, such a short immersion time is too short to reveal any degradation of the substrate.

The impedance data of patinated bronze samples after 1 hour immersion in simulated acid rain were fitted with the simple equivalent circuit consisting of only one time constant, presented in Figure 5a, and the resultant EIS parameters are given in Table 2. The impedance spectra were fitted using the ZSimpWin software. The fitting quality of EIS data was estimated by both the chi-square (χ^2) test (between 10^{-4} and 10^{-5}) values and the comparison between error distribution versus frequency values (± 2% for the whole frequency range) corresponding to experimental and simulated data. The R_{pore} and Q_c (*c* means coating) parameters describe the processes occurring at electrolyte/patining layer. R_{sol} is the ohmic resistance of the electrolyte.

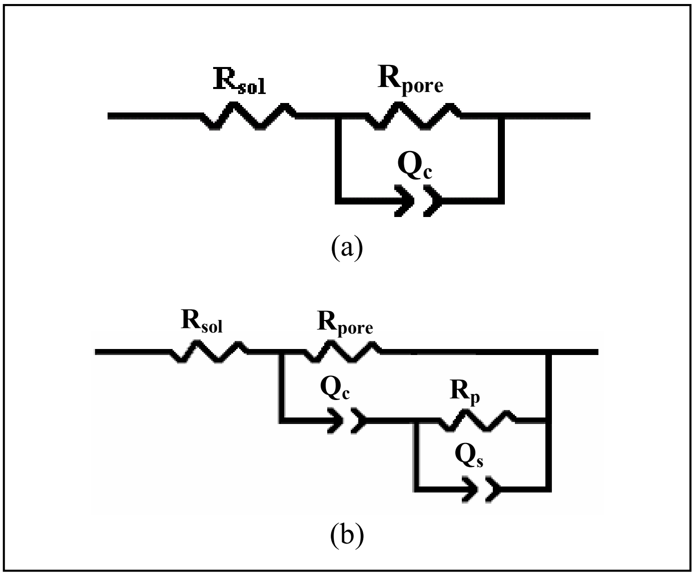

Figure 5. Equivalent circuits used for fitting the measured impedance spectra.

Table 2. Electrochemical parameters obtained from EIS spectra using the selected ECs for the patinated bronze sample in simulated acid rain at open circuit potential.

Immersion time	$10^5 Q_c$ ($S\ cm^{-2}\ s^n$)	n_c	$10^4 R_{pore}$, ($\Omega\ cm^2$)	$10^5 Q_s$, ($S\ cm^{-2}\ s^n$)	n_s	$10^5 R_p$, ($\Omega\ cm^2$)
1 hour	1.7	0.81	55.3	-	-	-
1 day	8.7	0.80	2.3	2.3	0.69	1.1
7 days	8.9	0.79	1.9	2.7	0.68	0.9
30 days	9.1	0.78	1.4	3.4	0.65	0.6

When the immersion period is greater than 1 day, the phase shift is different to that of 1 hour. The low-frequency domain evidences the processes taking place at the substrate/electrolyte interface. Such behaviour is typical for a metallic material covered with a porous film, which is exposed to an electrolytic environment. In this case, the electrochemical interface can be subdivided into sub-interfaces: electrolyte/patinated layer and electrolyte/substrate. This type of EIS spectra is best modelled by an equivalent circuit (EC) proposed by Liu et al [7] for the two sub-electrochemical interfaces, as shown in Figure 5b.

The parameter R_p coupled with Q_s (*s* means substrate) describes the processes at the substrate layer at the electrolyte/substrate layer interface. R_{pore} is the charge transfer resistance associated with the penetration of the electrolyte trough the pores or pinholes existing in the patining layer, and R_p is the polarization resistance at the electrolyte/substrate interface in the pores or pinholes. Q_c corresponds to capacitance of the patining layer and Q_s to the capacitance at the electrolyte/substrate layer interface which seem to be associated to the double layer formation.

Figure 6. SEM obserevation of the patinated sample after 30 days immersion in simulated acid rain.

The good R_{pore} value at the immersion time of 1 hour indicated a good capacitive response between simulated acid rain and patina surface and no degradation of the substrate was revealed. With the increase of immersion time, the advanced formation of occluded cells caused the increase of oxygen near patina surface. The decreases of R_{pore} as the immersion time increases imply that with the increased number of opening pore and pinholes the protective performance was weakened. The SEM image of patinated sample after 30 days immersion in simulated acid rain (Figure 6) confirms this aspect.

The improvement of conductive property for patina surface caused the decrease of R_p.

4. Conclusions

The failure process of the patining for bronze in simulated acid rain has been investigated. Electrochemical tests showed that the process failed was caused by the pores and pinholes in the film. The patining offered good protection for bronze substrate at the beginning of long-term immersion (small corrosion current density). With the increase of immersion time, the solution penetrated into the interface through the pores and pinholes, and the corrosion resistance of the patining failed.

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