STUDY OF PATINA DEPOSITION ON BRONZE ARTEFACTS EXPOSED TO ENVIRONMENTAL CORROSION IN OPEN SPACES

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Abstract

Corrosion and wearing of metal surfaces are the most common problems faced in industry as well as in environmental use. In the present study, two different protective artificial patina coating were deposited on bronze substrates. The linear polarization curves and electrochemical impedance spectroscopy have been employed to study the corrosion performance of the patinated bronze sample in acid rain. Equivalent circuits (EC) were used to model EIS data in order to characterize sample surface. In addition, scanning electron microscopy (SEM) was employed to observe the surface morphology before and after anodic polarization test. Thermal analysis was also performed on both witness and corroded samples. Substantial improvement of the corrosion resistance of patina coated bronze substrates was obtained by a spray test. On the basis of the important information obtained in this study, the protective properties of patina coatings can be tailored for bronze substrates.

Keywords: patina, simulated acid rain, SEM, EIS, thermal analysis

1. Introduction

The present study is a continuation of our previous works in the field of bronze artefacts corrosion [1-3]. In the present work we studied the electrochemical corrosion behaviour of patinas formed on bronze substrate by two methods in simulated acid rain.

The reason of our work concerns the fact that the bells are usually located outdoor, in open spaces, being subjected to the corrosion action of the environmental corrosion factors (e.g. acid rains).

Another aim of the article is to correlate, when possible, the thermal analysis data with those obtained by means of electrochemical methods.

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2. Experimental

The 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 first sample (Patina1) was patined for 24 hours into a sulfuric acid solution (30%) with a carbon dioxide current (1L/min). The second sample (Patina2) was patined by spraying with a solution containing: 13.5% NH_4Cl, 8.3% potassium tartrate, 10.8% NaCl, 13.5% $Cu(NO_3)_2$ and 54.1% H_2O until the formation of a compact green layer.

Corrosion tests were performed electrochemically at room temperature ($\sim$25°C) in a simulated acid rain.

The tests specimens was placed in a glass corrosion cell, which was filled with freshly prepared electrolyte. A saturated calomel electrode (SCE) was used as the reference electrode and a platinum coil as the counter electrode. All potentials referred to in this article are with respect to SCE. The measurement was managed by a VoltaLab 40 potentiostat controlled by a personal computer with dedicate software (VoltaMaster 4).

After the open circuit potential was held for 2 hours, the polarization test was performed. These tests were conducted by stepping the potential using a scanning rate of 1 mV/s from -600 mV (SCE) to +1000 mV (SCE).

EIS measurements were performed after the samples were immersed in simulated acid rain at 25$\pm$1°C, at open circuit potential, for different period of times: 1 hour, 2 hours and 24 hours. The alternating current (AC) impedance spectra for samples were obtained with a scan frequency range of 100 kHz to 10 mHz with amplitude of 10 mV.

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. The usual guidelines for the selection of the best-fit EC were followed: a minimum number of circuit elements are employed and the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the error associated with each element was up to 5%. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure to obtain good agreement between the simulated and experimental data [1, 3].

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.

Corroded and uncorroded samples of about 150-250 mg were submitted to TG/DTA analyses. The air supplied by a compressor (4–5 bar) was passed over granular silica gel. The nitrogen was supplied from Linde gas cilinder (150 bar) of 4.6 purity class (99.996%). Thermogravimetric analyses (TG and DTA) were performed under nitrogen or air flow (20 cm^{3}min^{-1}) at a heating rate of 10°C/min from 25 to 1000°C with a *Mettler Toledo model TGA/SDTA 851*.

3. Results and discussion

3.1. Microstructure and morphology

The planar SEM images of the Patina1-coated and Patina2-coated samples are shown in Figure 1 and the EDX analysis of both patina coatings are presented in Figure 2.

The microstructure of Patina1-coated reveals the coating defects such as micro-pits (Figure 1a). In the case of Patina2-coated, there are many macro-particles on the surface of the bronze substrate, as one can see from Figure 1b. These macro-particles are not uniform, which is characteristic of spray method.

Local compositional analysis (Figure 2) of the deposition products indicated that they were patina. The EDX spectrum of Patina1, attest the presence of oxygen on bronze patinated surface suggesting that the patina mostly contain metal oxides (Figure 2a). The Patina2 EDX spectrum reveals the presence of C, Cl and O indicating a more complex and consistent composition of the coating layer (Figure 2b). Obviously, these results are in good agreement with the SEM images.

The SEM images of Patina1-coated, Patina2-coated and uncoated surface bronze samples after linear potentiodynamic polarization test in acid rain solution at 25° C have confirmed the presence of uniform degradation for treated samples and the presence of localized corrosion for untreated sample.

3.2. Electrochemical characterization

Plots in semi-logarithmic scale of current densities corresponding to Patina1-coated, Patina2-coated and uncoated bronze samples in simulated acid rain solution at 25° C traced between -600 mV to 1000 mV with 1 mV/s potential sweep rate, are displayed in Figure 3. The average values zero corrosion potential (ZCP) and corrosion current density (i_{corr}) from polarization curves determined by the VoltaLab 4 software are presented in Table 1.

The linear polarization curves of Patina1-coated bronze showed a shift of ZCP to more negative value (-348 mV) compared with Patina2-coated and uncoated bronze (-64 mV, -96 mV). The lower ZCP exhibited for Patina1-coated bronze probably can be associated with the porous character of this coating. Probable the solution pH increases inside the pores and shift the cathodic reaction curve to lower potentials.

The corrosion current density was shifted to lower values in case of Patina1-coated and Patina2-coated bronze. The oxygen is essential for the growth of the passive film. In the case of Patina1-coated bronze, it is expect that the oxygen content inside the pores is smaller than the surface. As a result the anodic current show a monotonically increase near the zero corrosion potential.
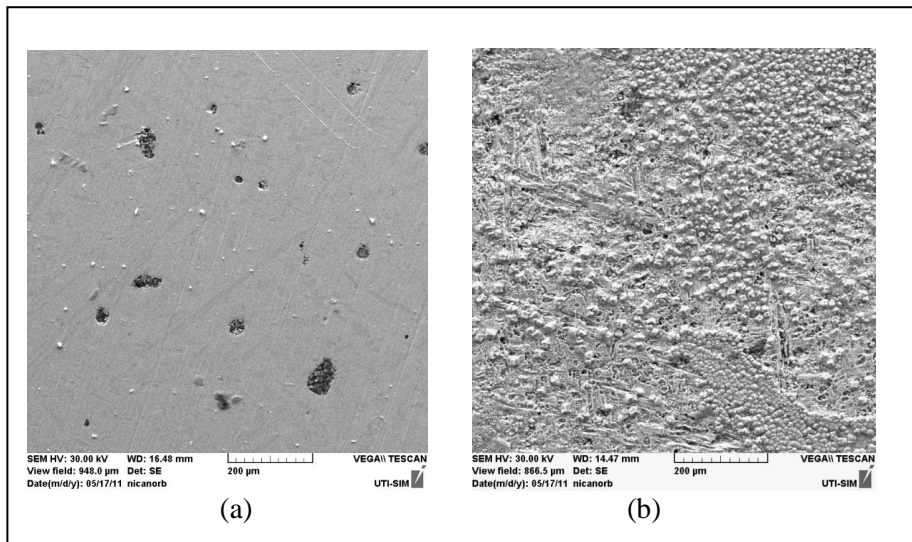
Figure 1. SEM images of: (a) Patina1-coated and (b) Patina2-coated samples.
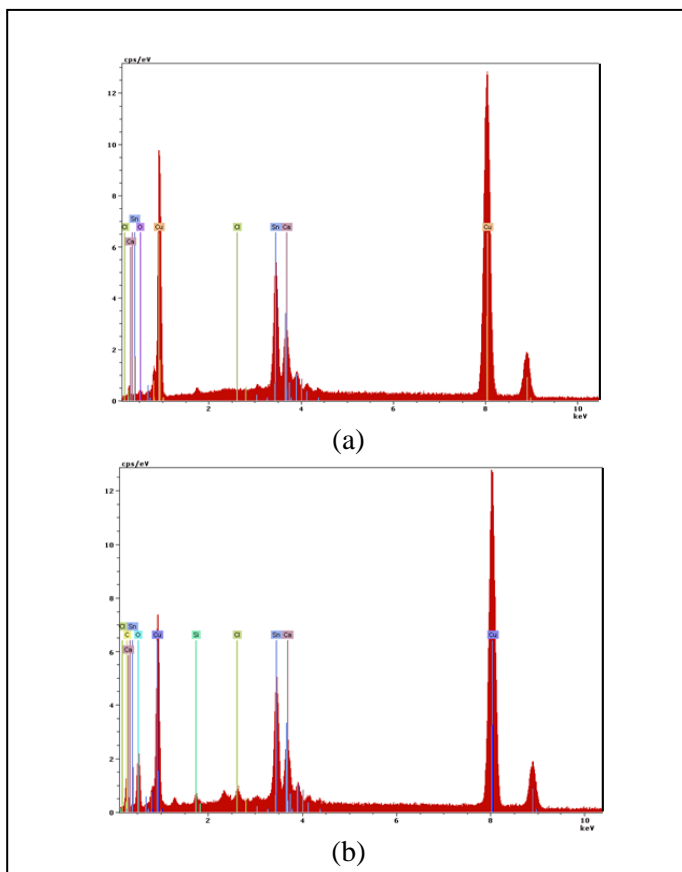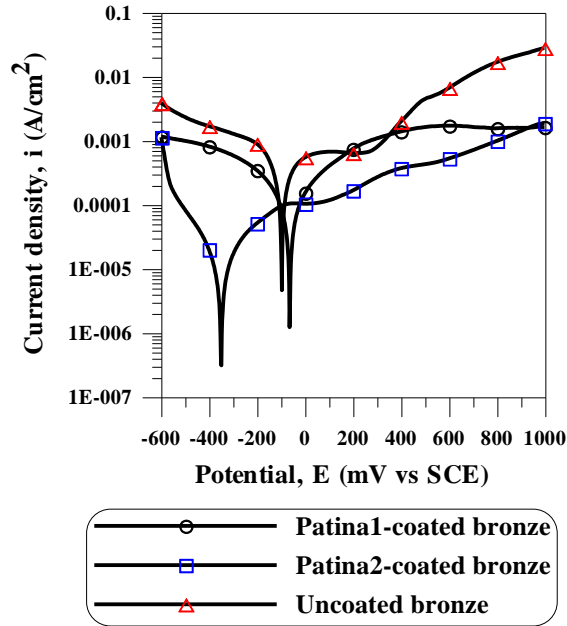

Figure 2. EDX spectrum of: (a) Patina1-coated and (b) Patina2-coated samples.

Figure 3. Linear potentiodynamic polarization curves measured for Patina1-coated, Patina2-coated and uncoated bronze specimens in simulated acid rain solution.

Table 1. The mean values of parameters measured and calculated for the samples in acid rain solution at 25° C.

Sample	ZCP (mV)	i_{corr} ($\mu A/cm^2$)	E_{bd} (mV)	E_{bd} -ZCP (mV)
Unpatinated bronze	-375	2.5	312	408
Patina1-coated bronze	-348	230	-	-
Patina2-coated bronze	-64	55	-	-

Uncoated bronze translated directly into stable passive behaviour from 'Tafel region'. Above 300 mV, the passive film breakdown takes place.

The susceptibility of an alloy to localized corrosion in a certain medium can be characterized in terms of the breakdown potential (E_{bd}) relative to the ZCP [4, 5]. The potential range situated between the ZCP and E_{bd} represents the passivity zone in which corrosion is weak or even insignificant. Thus, the difference between the E_{bd} and the ZCP, is commonly used as a measure of the material's susceptibility to pitting corrosion. As the difference between, E_{bd} and ZCP becomes smaller, the alloy is expected to become more susceptible to pitting corrosion.
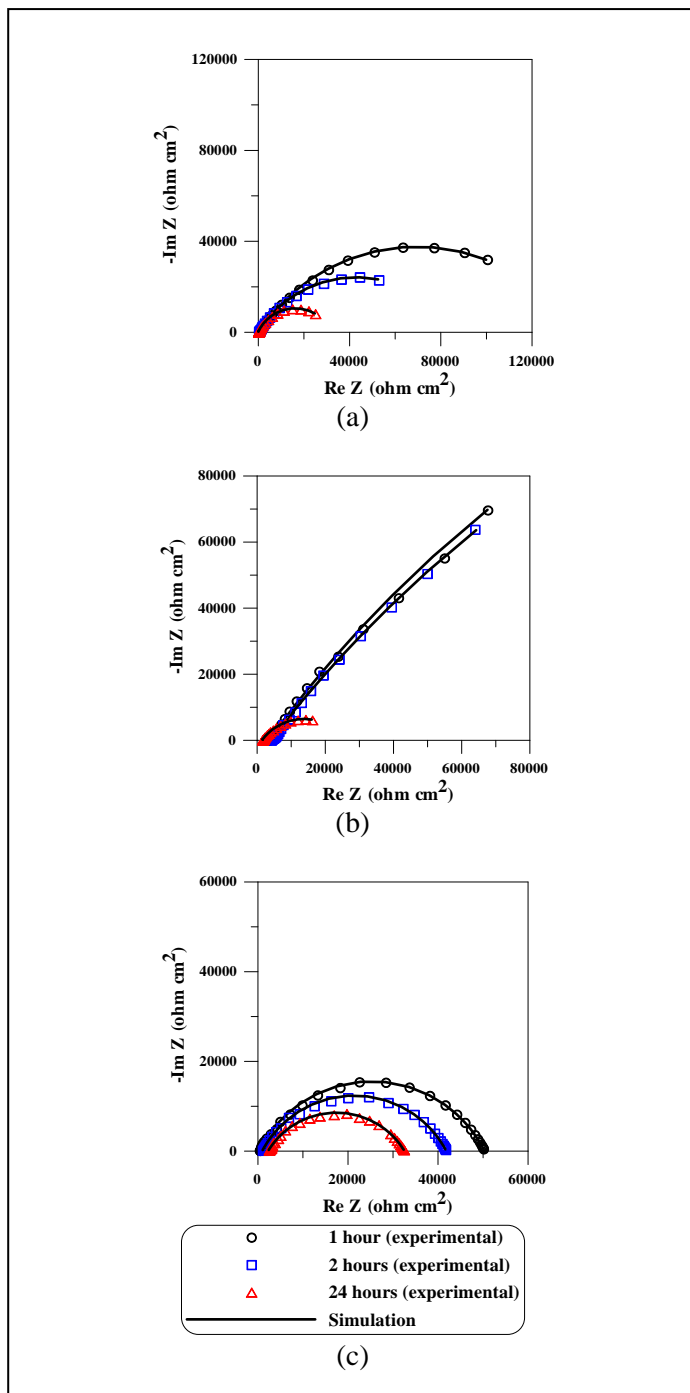
Figure 4. Electrochemical impedance diagrams for: (a) Patina1-coated, (b) Patina2-coated and (c) uncoated bronze as a function of immersion time in aerated simulated acid rain.

The Nyquist impedance diagrams for Patina1-coated, Patina2-coated and uncoated bronze obtained in aerated acid rain as a function of immersion time are shown in Figure 4.

When a protective surface layer is formed on metal, the metal's impedance show in the EIS plot predominantly corresponds to the capacitive effect of surface passive layer because the capacitive effect of the metal's charge transfer reaction is smaller. All the diagrams for coated bronze show a capacitive arc. The capacitive arc may be related the dielectric properties of the coated film on the electrode surface at open circuit potential. In the case of uncoated bronze, the capacitive arc may be related the electric double layer capacitance at the electrode/solution interface, which includes a passive film-solution interface. The diameters of the semicircles correspond to the polarizing resistance (R_p) indicative of the kinetics of the charge transfer reactions or rate of dissolution. It could be observed from the Figure 4 that after 1 day of immersion in simulated acid rain, the diameter of the semicircle all the samples (coated and uncoated) decreased. The decrease in diameter indicates a decrease in corrosion resistance.
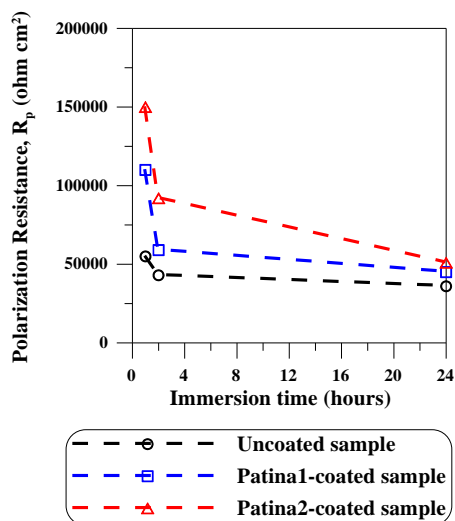
Figure 5. Polarization resistance (R_p) of coated and uncoated bronze samples maintained different time periods in simulated acid rain measured at open circuit potential.

The R_p obtained the Convertor and ZSimpWin software to the experimental EIS data, are manifested in Figure 5. The Randles equivalent circuit (EC) was used to model the experimental spectra, and good agreement between experimental data and fitted data was obtained. 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 ($\pm$ 5% for the whole frequency range) corresponding to experimental and simulated data. After 1 hour immersion time, corrosion resistances are higher for coated

sample than for uncoated sample. The Patina1-coated bronze has the resistance of polarization about three times higher than the uncoated bronze sample. It showed that the R_p decreased with increasing the immersion time for all samples (coated and uncoated). However the values of polarization resistance measured for all the samples after 24 hours of immersion are around 5×10^4 Ω cm^2. EIS results give the experimental evidence that coatings are not very dense and present defects.

3.3. Thermal analysis

The preliminary thermal analysis data for the untreated and for the coated samples are listed in Table 2.

The first peculiarity of the analysed material is the fact that it gains in weight, in nitrogen atmosphere but not in air, at low temperatures (between 50 and 220°C). As somehow expected the mass increase is higher when the material has a larger specific surface (shavings). Obviously, at higher temperatures (over 700°C), in air, the mass increase is much higher due to oxidation processes. At about 510°C an endothermic phase transformation occurs.

Table 2. TG and DTA data for the analysed materials.

Sample	T_1 (°C) Mass var. (%) DTA	T_2 (°C) Mass var. (%) DTA	T_3 (°C) Mass var. (%) DTA	T_4 (°C) Mass var. (%) DTA	T_5 (°C) Mass var. (%) DTA
Bulk in N$_2$	51.57-210.45 + 0.06 -	-	330.89 + 0.02 -	452.09 + 0.01 528.33 (endo)	869.8 + 0.08 785.45 (endo)
Bulk in air	-	-	- 515.73 (endo)	751.03 + 0.35 786.51 (endo)	896.49 + 6.07 880 (endo)
Shavings in N$_2$	56.91-220.17 + 0.18 -	-	368.12/DTG + 0.12 -	495.65 + 0.07 515.21 (endo)	545.62-952.2 + 0.35 784.51 (endo)
Shavings in air	-	-	- 512.65 (endo)	695.97 + 7.03 698.34 (exo)	847.42 + 16.22 816.67 (exo)
Patina1 in N$_2$	78.38 - 0.01 -	90.85-226.52 + 0.007 -	339.16 - 0.009 -	459.25-972.45 + 0.092 519.93/787.4 (endo)	
Patina2 in air	253.87 - 1.87 264.31 (exo)	427.87 + 1.18 403.8 (exo)	526.82 + 0.99 517.43 (endo)	684.09 + 1.58 660.24 (exo) 784.64 (endo)	892.46 + 1.76 884.06 (exo)

The Patina1 sample has a very low mass decrease comparing with Patina2 in the lower temperature region. This behaviour is in agreement with the EDX and SEM analyses, the Patina1 coating surface containing almost no water due to the fact that is constituted from metal oxides (especially of copper). On the other hand, at higher temperatures, in air, Patina2 has a low mass variation compared with the untreated sample, indicating the formation of a quite good protective layer.

However, as expected, one must notice that the chemical processes that occur during the heating are very complex, the decomposition of certain compounds superimpose with oxidation processes and phase transformations, making the whole picture very difficult to elucidate in its intimate developing.

4. Conclusions

This preliminary study indicates that the two proposed coating methods provide corrosive protection for the bronze material. However, Patina2 is much resistant to the environmental corrosion action than Patina 1.

It is also remarkable that fact that the thermal analysis data are in quite good agreement with the electrochemical data. This is also noticeable if we are taking into account that this correlation is in its early stage and there are only a few studies performed in the field.

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