ELECTROCHEMICAL BEHAVIOUR OF SOME RELIGIOUS ARTEFACTS IN SIMULATED ACID RAIN

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Abstract

The aim of this study was to investigate the effects of immersion time on the electrochemical corrosion behaviour of three brass alloys in simulated acid rain at 25°C, utilizing the electrochemical impedance spectroscopy (EIS). The main parameters of the corrosion process were established. The immersion of the alloys in simulated acid rain reduces the intensity of the corrosion process. For all the samples the polarization resistance (R_p) is increasing with the immersion, from 1 minute to 1 hour and 1 day respectively. The EIS results exhibited relative capacitive behaviour (suitable corrosion resistance) with phase angle close to -70° and relative large impedance values (order of 10^4 Ω cm^2) at low and medium frequencies, which are indicative of the formation of a stable oxide film on these brass samples in simulated acid rain. Equivalent circuits (EC) were used to modeling EIS data, in order to characterize samples surface.

Keywords: brass alloys, simulated acid rain, corrosion, SEM, EIS

1. Introduction

For the conservation − restoration field, a pollutant is defined as any reactive chemical compound in a gaseous, liquid or particulate state found in the preservation environmental of art objects. These agents of deterioration may interact with the materials of objects and artefacts in ways that greatly accelerate their deterioration.

The damage inflicted on museum objects by atmospheric pollutants has been observed almost since the dawn of the industrial era. More than 150 years ago, the deleterious effects of soot and sulphur dioxide were observed on paintings at the National Gallery in London, and glazing was installed over works of art to protect them [1].

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A great deal of actual research into the effects of pollutants has been conducted due the concern for the exterior environment or with the effects on human health rather than on materials. 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 [2].

It is difficult to identify the lowest level of pollutants as which damage to materials can occur, because the often synergistic effect of environmental pollutants, relative humidity (RH) and the extreme variability of materials housed in collections. Depending upon the chemical species involved, the deterioration process may be irreversible and permanent, or only temporary, subject to changes in RH, temperature, or the introduction of additional pollutant species [1, p. 5].

It is known that the local control of moisture vapour plays a vital role in the preservation of metal artefacts. Corrosion develops under thin layers of adsorbed oxygen and water and only a few adsorbed molecular layers of moisture are required for corrosion to proceed [3].

In recent years, the susceptibility of Fe, Cu, Ag and bronze, as constituent materials of art object, to corrosion due pollutants agents are referenced as well [4-7]. However, the complicate nature of interaction between pollutants and their ability to enhance the deterioration or corrosion process is not completely understood.

By rapid electrochemical tests we can monitory the samples, at least in the qualitative way, with respect to their corrosion resistance.

The electrochemical methods based on the open circuit potential and polarization curves recording are frequently used. Direct current (DC) electrochemical methods are commonly used to evaluate corrosion, but over the past decade many articles on the electrode impedance spectroscopy (EIS) have been published and was demonstrated that the alternative current (AC) impedance method is particularly useful when monitoring some electrochemical changes as a function of time, being a non-destructive technique [8-11].

Consequently, our study is dealing with three brass alloys (CuZn), and their corrosion behaviour in simulated acid rain.

2. Experimental

2.1. Materials

Table 1. Chemical composition of the investigated brass samples.

	Composition (wt %)
Samples 1	Cu: 63, Zn: 37
Samples 2	Cu: 61, Zn: 36, In: 3
Samples 3	Cu: 57, Zn: 32, Ni: 11

The brass alloys analyzed has the compositions presented in Table 1.

2.2. The electrochemical media

The composition of simulated acid rain [12] is shown in Table 2.

Table 2. Composition of the simulated acid rain.

| Ion	Concentration (mg/L)
F^-	0.098
Cl^-	2.0
NO_3^-	7.1
SO_4^{2-}	10.9
Na^+	0.42
K^+	0.11
Ca^{2+}	0.049
Mg^{2+}	0.051

2.3. Electrochemical tests

Electrochemical measurements were carried out at $25 \pm 1^{\circ}C$. The working electrode, processed in cylindrical shape and mounted in a tetrafluoroethylene support, presents a one-dimensional circular area surface exposed to corrosion.

The sample was cut to 1.9 cm^2 size and the brass nut was attached to each sample using conductive paint to ensure electrical conductivity. The assembly was then embedded into an epoxy resin disk. Then the sample was ground with SiC abrasive paper up to 2000 grit, while the final polishing was done with 1 μm alumina suspension. The sample was degreased with ethyl alcohol followed by ultrasonic cleaning with deionised water and dried under a hot air stream.

The electrochemical measurements were made with a potentiostatic assembly of three electrodes: a working electrode, a platinum counter-electrode and a reference electrode of saturated calomel (SCE). All potentials referred to in this article are with respect to SCE. The measurement system was managed by a VoltaLab 40 potentiostat controlled by a personal computer with dedicate software (VoltaMaster 4).

Electrochemical impedance spectroscopy (EIS) was used to evaluate the corrosion resistance of the samples. The EIS spectra were obtained at 1 minute, 1 hour and 1 day after the electrode was immersed in the solutions. The alternating current (AC) impedance spectra for brass alloys 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.
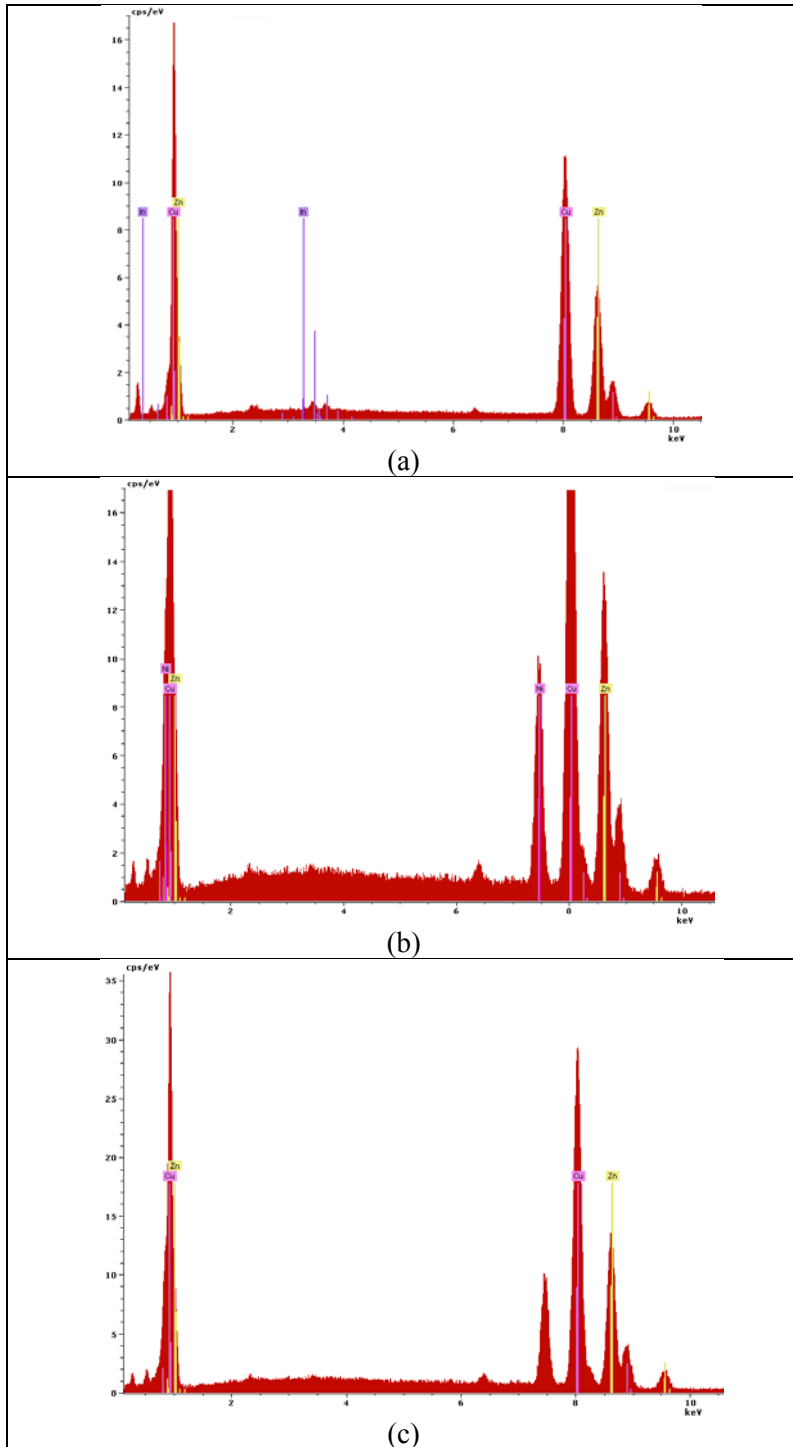
Figure 1. EDX spectrum for brass alloys surface: (a) sample 1, (b) sample 2, (c) sample 3.
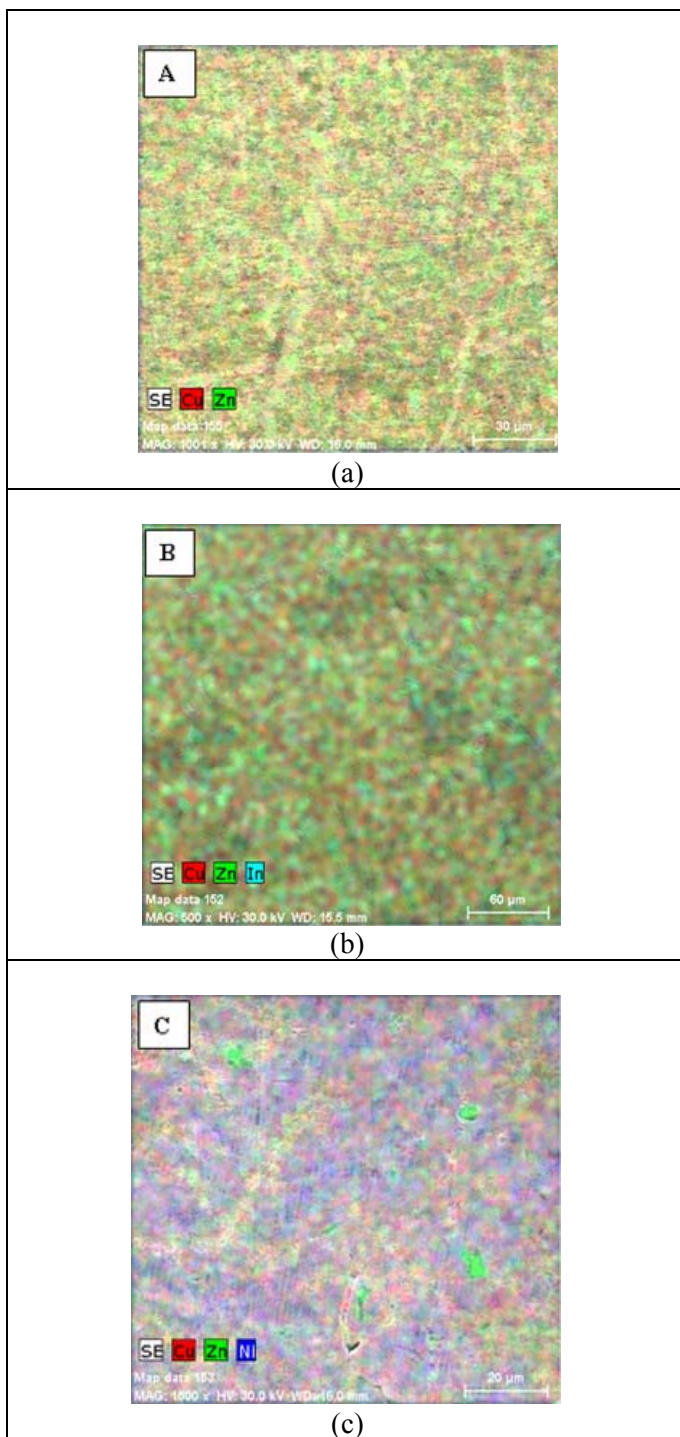
Figure 2. The map distribution elements to brass alloys surfaces: (a) sample 1, (b) sample 2, (c) sample 3.

2.4. Surface characterization

The brass alloys surface were investigated using a Vega Tescan scanning electron microscope (model VEGA II LMH) having detector (model xflash, Bruker) for EDX analysis.

3. Results and discussion

3.1. EDX analysis

The EDX spectrum for the brass alloys surface confirms the presence of: Cu and Zn in the case of sample 1, Cu, Zn and In in the case of sample 2, and Cu, Zn and Ni in the case of sample 3 (Figure 1). The map of distribution elements to brass alloy surfaces is shown in Figure 2.

3.2. Open circuit potential

Figure 3 shows the values of open circuit potential after 1 minute, 1 hour and 1 day immersion of brass alloys in simulated acid rain.

The examination of Figure 3 shows immediately that the variation of open circuit potential with times on immersion in simulated acid rain is the same for all brass alloys. The potential moved towards noble potentials on immersion. In all cases, the change of open circuit potential with time is accompanied by the formation of a film of corrosion products seen by visual inspection. It is likely that the main constituent of the film is cooper oxide.
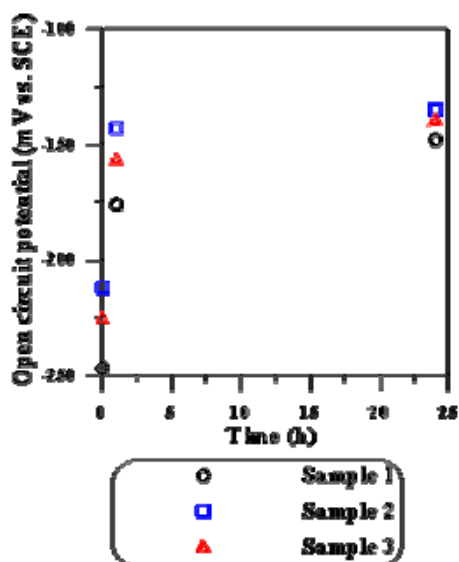
Figure 3. Open circuit potential data recorded on brass alloys for different immersion times at 25ºC in simulated acid rain.

3.3. Electrochemical Impedance Spectroscopy

The corrosion resistance can be estimated by means of the impedance method known as Electrochemical Impedance Spectroscopy (EIS). This technique requires minimal invasive procedures; neither the oxidation nor the reduction was forced to take place in the open circuit mode. From the EIS data we can obtain information about the passive film dissolution (the rate and type of the control) and the passive film characteristics (film thickness, passive film dielectric constant, diffusion coefficient of the diffusing species etc.)

Figures 4 shows the EIS data, in the form of Bode plot, of all brass alloys at open circuit potential, after 1 minute, 1 hour and 1 day of immersion in simulated acid rain.

The advantage of the Bode plot is that the data for all measured frequencies are shown and that a wide range of impedance values can be displayed. From the Bode spectra it is possible to indicate the presence of a compact passive film if:

- the phase angle is close to -90° over a wide frequency range,
- if the spectrum shows linear portions at intermediate frequency.

Generally, three frequency regions referring to the high, intermediate and low frequency values are obtained from impedance spectra. This high frequency plateau of the impedance values at frequency $>10^4$ Hz, with the phase angle approaching 0, yields the value of the electrode ohmic or solution resistance, R_{sol}. The intermediate frequency region (10^3 to 10 Hz) has the maximum phase angle and the logarithm of impedance versus logarithm of the frequency slope approaching -1. Those impedance responses correspond to the capacitive behaviour of the electrode and describe the dielectric properties of the electronically conducting surface film. The low frequency region (frequency < 10 Hz) detects the mass transfer (diffusion or migration) processes, or other relaxation processes taking place at the film-electrolyte interface or within the pores of the surface film.

All spectra show that in a higher frequency region, log Zmod tends to become constant. This is a typical response of the resistive behaviour and corresponds to the solution resistance, $R_{sol.}$. The slopes and the phase angle increase with increasing of the immersion time. The increase in the impedance value observed for 1 day of immersion indicated an increase in corrosion resistance of the oxide film.

For the interpretation of the electrochemical behaviour of a system from EIS spectra, an appropriate physical model of the electrochemical reactions occurring on the electrodes is necessary. The electrochemical cell, because it presents impedance to a small sinusoidal excitation, may be represented by an equivalent circuit (EC). An EC consists of various arrangements of resistances, capacitors and other circuit elements, and provides the most relevant corrosion parameters applicable to the substrate/electrolyte system.
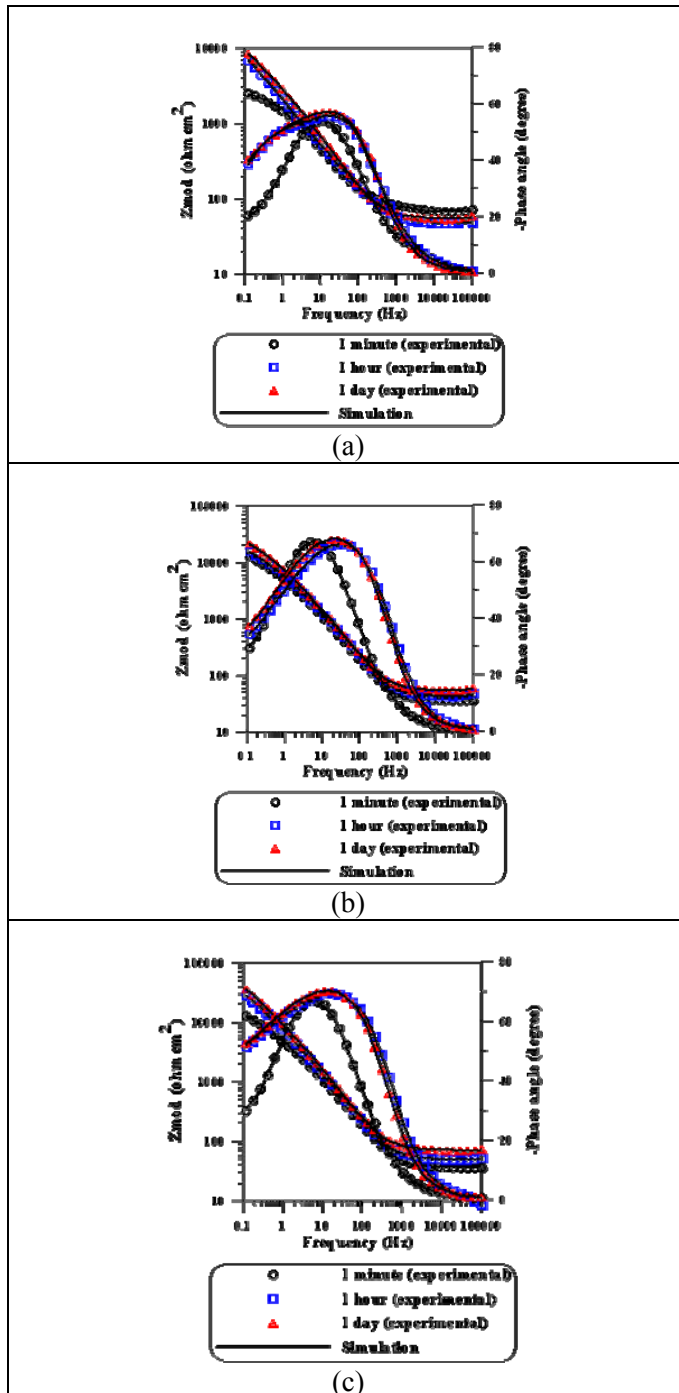
Figure 4. Bode plots recorded at open circuit potential after immersion for 1 minute, 1 hour and 1 day in simulated acid rain: (a) sample 1, (b) sample 2, (c) sample 3.

The usual guidelines for the selection of the best-fit EC were followed:
- a minimum number of circuit elements were to be employed,
- the χ^2 error was suitably low ($\chi^2 < 10^{-4}$), and the error associated with each element were up to 5%.

The EC that satisfied the above criteria was used to fit the experimental data and is presented in Figure 5. Instead of pure capacitors, constant phase elements (CPE) were introduced in the fitting procedure in order to obtain good agreement between the simulated and experimental data. The impedance of the CPE is given by [13]:

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

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 ($j^2 = -1$).

The impedance data of all brass alloys after 1 minute of immersion in simulated acid rain were fitted with the EC presented in Figure 5a, and the resultant EIS parameters are given in Table 3. The value of R_1 representing the charge transfer resistance (R_{ct}) is quite low (order of 10^3 Ω cm^2) and indicates the low stability of brass alloys after 1 minute immersion in simulated acid rain. Charge transfer resistance (R_{ct}) is defined generally for kinetically controlled electrochemical reaction. The element Q_1 represents the double layer capacitance (C_{dl}) as shown by the high value of the n_1 exponent (around 0.85).
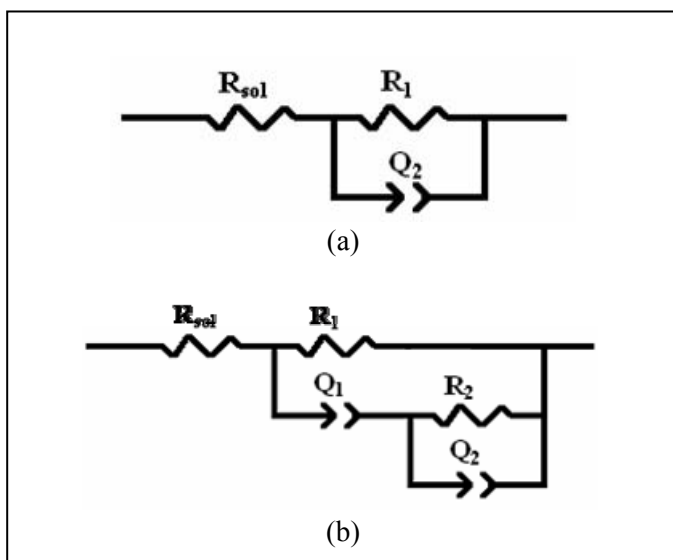
**Figure 5.** Equivalent circuits (EC) used to fit the impedance data.

Table 3. Impedance parameters for brass alloys in simulated acid rain at open circuit potential.

	R_1 (kΩ cm^2)	$10^5 Q_1$ (S cm^{-2} s^n)	n_1	R_2 (kΩ cm^2)	$10^5 Q_2$ (S cm^{-2} s^n)	n_2
The samples maintained for 1 minute in test solution						
Sample 1	4.6	2.2	0.84	-	-	-
Sample 2	7.9	1.9	0.85	-	-	-
Sample 3	8.4	1.5	0.85	-	-	-
The samples maintained for 1 hour in test solution						
Sample 1	1.1	1.1	0.86	8.5	2.9	0.65
Sample 2	1.1	1.3	0.87	19	2.6	0.68
Sample 3	1.2	1.2	0.87	22	2.5	0.71
The samples maintained for 1 day in test solution						
Sample 1	1.2	1.2	0.87	9.8	1.9	0.67
Sample 2	1.2	1.2	0.87	22	2.3	0.71
Sample 3	1.2	1.1	0.88	34	2.3	0.71

In case of brass alloys after 1 hour and 1 day of immersion in simulated acid rain at open circuit potential the Bode-phase plots are in agreement with an EC with two time constant. The EC (Figure 5b) contains two RQ elements in parallel: $R_{sol}(Q_1(R_1(R_2Q_2)))$. Other combinations of resistance and capacitances were tried, in particular one RQ elements in parallel: $R_{sol}(R_1Q_1)$ or two RQ parallel combinations: $R_{sol}(R_1Q_1)(R_2Q_2)$, to model the corrosion process of samples in simulated acid rain, but none of these were found to give a satisfactory fit (values of chi-square (χ^2) test were about 10^{-2}).

In these cases a formation of a film of corrosion products was seen by visual inspection. This justifies the use of $R_{sol}(Q_1(R_1(R_2Q_2)))$ circuit to model EIS data.

The two RQ elements can be attributed to charge transfer at the metal-oxide film interface and to the oxide layer formed on the surface. The double layer capacitances for all samples are typical for the (C_{dl}) of the oxide layers [14-17]. The same value for cell resistance, R_{sol}, equals 45 ± 5 Ω, was observed for all of the specimens indifferent the time of immersion and it wasn't inserted in Table 3.
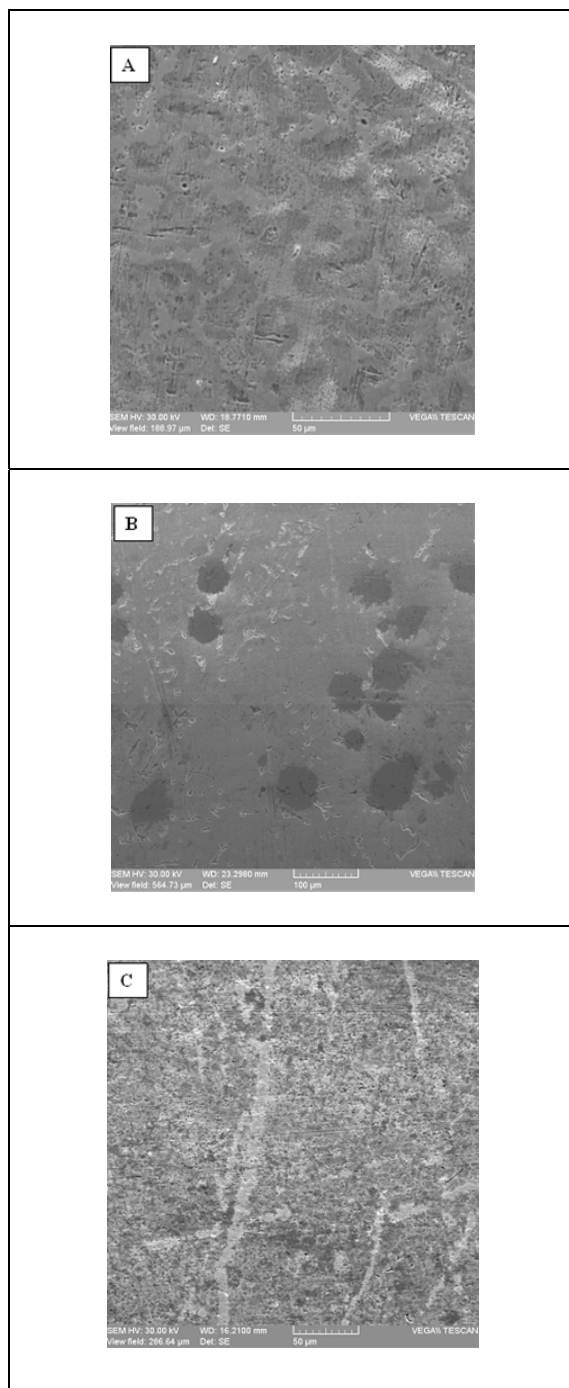
Figure 6. SEM observations of: (a) sample 1, (b) sample 2 and (c) sample 3 after 1 day immersion in simulated acid rain.

In Figure 4, the experimental data are shown as individual points, while the theoretical spectra resulting from the fits to a relevant EC model are shown as lines.

The overall polarization resistance R_p is represented by the sum of partial resistance $(R_1 + R_2)$ [18]. R_p allows a quantitative analysis based on the specific magnitudes of the corrosion rate. R_p is related to the rate of corrosion reaction(s) and is inversely proportional to the corrosion current; the Stern-Geary equation [19]:

$$i_{corr} = \frac{b_a b_c}{2.3 R_p (b_a + b_c)} = \frac{B}{R_p} \tag{2}$$

where: b_a and b_c are the Tafel slopes for the partial anodic and cathodic processes, respectively and B is a constant:

$$B = \frac{b_a b_c}{2.3(b_a + b_c)} \tag{3}$$

The polarization resistance for all brass alloys increases with time after 1 hour of immersion. This phenomenon must be associated with the formation of the protective oxide film on the surface of the all samples. For the brass alloys after 1 hour and 1 day of immersion in simulated acid rain the values of n_2 are small, in the range of 0.65-0.7 indicating the presence of a diffusion process within the interfacial layer of the solution.

Such a diffusion process indicates a reversible dissolution process; i.e. the oxide film formation under open circuit condition proceeds through a dissolution-precipitation mechanism [20].

The oxide film presents a protective character and the polarization resistance increases with the immersion time, probably because the oxidation kinetics process is diffusion controlled associated to mass transport of the ions inside the film pores. The corrosion resistance of the three brass alloys decreases in the following order: sample 1 > sample 2 > sample 3. It is probable that alloying addition of In (sample 2) and Ni (sample 1) results in improved resistance to active dissolution in simulated acid rain.

3.4. SEM surfaces

Figure 6 shows the surface micrographs of brass alloys after 1 day immersion in simulated acid rain. The analysis of Figure 6 indicates the appearance of corrosion points at the surface of sample 2, and the development of a uniform corrosion process in case of sample 1 and sample 3.

4. Conclusions

Electrochemical testing as an investigation method of ancient and historic metal has the potential to replace the subjective, visual assessment of degree of corrosion associated with the Oddy test [21] in the evaluation of material state of conservation.

The EIS results exhibited relative capacitive behaviour (good corrosion resistance) with phase angle close to −70° and relative large impedance values (order of 10^4 Ω cm^2) at low and medium frequencies, which are indicative of the formation of a oxide layer on these alloys after 1 hour and 1 day of immersion in simulated acid rain. The EIS analysis has shown that the resistance of the oxide film formed on brass alloy samples increased with immersion time. Equivalent circuits were proposed to electrochemical behaviour of all brass alloys in simulated acid rain. Using EIS technique, it was found that the alloying CuZn alloy with 3% In and 11% Ni increases the polarization resistance.

As the role of environmental factors in the deterioration of metal art object will become better understood the preoccupation of conservators will move to the treatment damage already sustained to prevention the future damage effects.

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