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EVALUATION OF SOME AMINO ACIDS AS BRONZE CORROSION INHIBITORS IN AQUEOUS SOLUTION

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ABSTRACT. A comparative study of the efficiency of two innoxious amino acids derivatives (DL alanine and DL cysteine) on bronze corrosion in 0.2 g/L $NaHCO_3$ +0.2 g/L Na_2SO_4 aqueous solution (pH 5), was studied by electrochemical impedance spectroscopy and polarization measurements.

The two amino acids are non-hazardous towards human beings or the environment and are intended to be used as corrosion inhibitors in the stabilization treatments of the Bronze Age archaeological artefacts belonging to the National Museum of Union in Alba Iulia (Romania). Consequently, the composition of the contemporary bronze samples used in the corrosion testing was chosen close to that of several Bronze Age artefacts (XII^{th} century B.C.) discovered in Transylvania (Romania) after a preliminary investigation by X-ray fluorescence spectrometry.

The electrochemical investigations showed that the two innoxious amino acids have fairly good inhibiting properties for bronze corrosion, acting mainly as cathodic inhibitors. Their inhibition action could be attributed to the ability of the amino acids to adsorb on the bronze surface and to form an organic layer which protects the metal from corrosion. In the investigated experimental conditions, the best protection of bronze was obtained in the presence of 0.1 mM cysteine (90%). The impedance measurements revealed that the inhibitor effectiveness of the optimal concentrations of amino acids is time-dependent.

Keywords: *bronze, corrosion, non toxic corrosion inhibitors, amino acids*

INTRODUCTION

The conservation and preservation of the cultural heritage is one of the main concerns within Europe today. Among the family of ancient and historical metals, bronzes artefacts that represent a considerable part of the archaeological findings, have been largely studied [1-3], because of their complex degradation phenomena, taking place in the long time span.

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Generally, upon excavation, the sudden change of environment, and sometimes the exposure to a more aggressive condition like polluted urban atmosphere induces the restarting of corrosion [1-6]. Consequently, in order to preserve the archaeological artefacts from corrosion, suitable treatments with coating substances are required. To this regard, in the late fifties and early sixties of the last century, a range of organic corrosion inhibitors, mainly nitrogen and sulphur-containing organic heterocyclic compounds, developed for industry, were tested as corrosion inhibitors of copper and bronze historical objects [7-12]. Among them, benzotriazole (BTA) has been widely accepted in the consolidation of the ancient copper and bronze artefacts being considered as the most efficient corrosion inhibitor over a wide temperature and pH range. Although, recent studies showed that BTA is highly toxic [12], being a cancerigen compound that cannot be degraded.

Therefore, in line with the environment protection regulations, the new trend in industry, as well as, in the conservation–restoration practice is nowadays orientated toward finding new environmentally friendly inhibitors, compounds with good inhibition efficiency of bronze corrosion, but with low risk of pollution [10-13].

When studying the cultural heritage objects, due to their unique nature and value, the evaluation of the efficiency exerted by the new proposed inhibitors for the protection of the authentic artefacts is much complicated and requires a special experimental methodology [14]. Thus, it is considered inappropriate to apply the novel anticorrosive treatments directly on the metallic surface without a preliminary screening, because the new inhibitors might irreversibly damage the ancient object either after the first treatment, or in time. Therefore, test procedures based on non-archaeological materials having a similar composition to the ancient ones are required. In this way, the effects of the new corrosion inhibitors could be studied without damaging the authentic artefacts.

In this context, the present work focuses on a preliminary investigation of the inhibiting behaviour of two amino-acids (cysteine and alanine) on bronze corrosion in an aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) by potentiodynamic polarization (Stern-Geary interpretation) and electrochemical impedance spectroscopy. These substances are nor toxic, neither noxious towards human beings or the environment and have already been reported as efficient corrosion inhibitors of copper in acidic and neutral solutions [13, 15-16]. They are intended to be used as corrosion inhibitors in the stabilization treatments applied on the Bronze Age archaeological artefacts belonging to the National Museum of Union in Alba Iulia (Romania).

The composition of the non-archaeological bronze used as working electrode in the corrosion testing was selected after a preliminary investigation on the chemical composition of several authentic Bronze Age artefacts discovered in Transylvania (Romania).

RESULTS AND DISCUSSION

Polarisation curves

The anodic and cathodic polarisation curves for bronze corrosion after 1-hour immersion in the corrosive solution in the absence and in the presence of various concentrations of amino acids are presented in Figure 1.

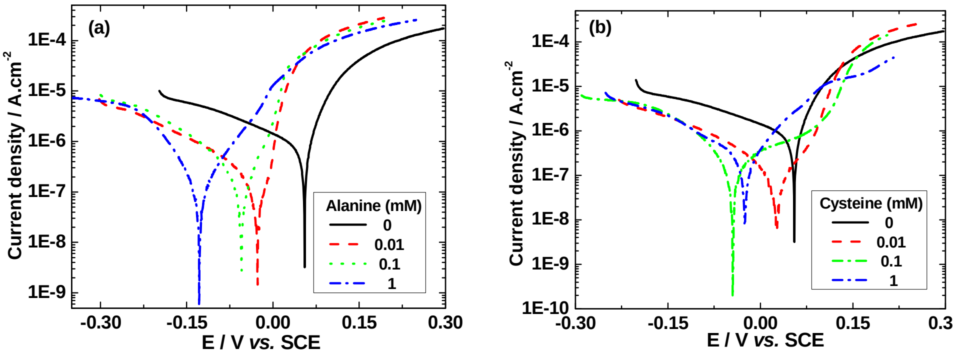

Figure 1. Polarisation curves for bronze in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) in the absence and in the presence of different concentrations of amino acids: (a) alanine; (b) cysteine. Scan rate, 10 mV/min.

As can be seen in Figure 1 and Table 1, the addition of the two amino acids gives rise to a decrease of the cathodic current densities as compared to the blank solution, in the whole applied potential range. Moreover, a shift of the corrosion potential towards more negative values was put on evidence both, in the presence of alanine and cysteine. This effect is more pronounced as the inhibitors concentration increases and suggests that the two organic compounds act mainly as cathodic-type inhibitors for bronze corrosion in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) solution.

The electrochemical corrosion kinetic parameters, *i.e.* corrosion potential (E_{corr}), cathodic activation coefficients (b_c, b_a) and corrosion current density (i_{corr}) were evaluated according to the equation:

$$i = i_{corr}\{\exp[b_a(E - E_{corr})] - \exp[b_c(E - E_{corr})]\} \qquad (1)$$

The values of the corrosion parameters in the absence and in the presence of different concentrations of amino acids calculated from the polarization curves are presented in Table 1.

In all cases, the correlation factor R^2 varies between 0.9896 and 0.9989 indicating a good fitting result.

The significant change of the cathodic Tafel coefficients in the presence of the amino acids as compared with the b_c value obtained in inhibitor-free solution suggests that the two organic compounds affect mainly the cathodic reduction of the oxygen, which is in good agreement with the shift of the corrosion potential in the cathodic domain. However, a slight influence of the amino acids on the anodic dissolution of the copper could also be observed.

Table 1. Corrosion parameters for bronze in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) without and with the addition of different concentrations of amino acids

Inhibitor conc.(mM)	**E_{corr} (mV/SCE)**	**i_{corr} (μA/cm^2)**	**b_a (V^{-1})**	**- b_c (V^{-1})**	**IE (%)**
0	47.80±0.4	1.26±0.03	39.44±0.29	7.68±0.23	-
Alanine 0.01	-24.57±0.4	0.23±0.030	37.50±5.17	11.44±2.13	81.75
0.1	-50.05±0.3	0.17±0.004	39.78±0.67	22.05±0.28	86.51
1	-116.55±0.1	0.31±0.001	27.08±0.36	20.93±0.11	75.40
Cysteine 0.01	36.02±0.6	0.14±0.002	35.23±0.85	17.08±0.21	88.89
0.1	-40.09±0.4	0.12±0.004	14.65±0.20	22.97±0.33	90.47
1	-25.01±0.2	0.26±0.004	28.33±0.14	16.64±0.16	79.36

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The corrosion inhibition efficiency (IE) at different concentrations of amino acids was calculated according to following equation [10]:

$$\mathrm{IE}(\%) = 100 \cdot \frac{i^0_{corr} - i_{corr}}{i_{corr}} \qquad (2)$$

where i^0_{corr} and i_{corr} are the values of the corrosion current densities in absence and in presence of the inhibitor, respectively.

The values of inhibition efficiency presented in Table 1 reveal that the investigated amino acids have inhibiting properties on bronze corrosion. A possible explanation for the inhibiting behaviour of the two amino acids could be found in their ability to adsorb on the bronze surface and to form an organic layer that protects the metal from corrosion.

The inhibition efficiencies increase as the inhibitors concentration increases and reach the maximum values in the presence of 0.1 mM alanine (86.95%) and 0.1 mM cysteine (90.47%). The further increase of the amino acids concentration in the corrosive solution leads to a decrease of their inhibition efficiency. This phenomenon is consistent with the results already reported for the copper corrosion in the presence of cysteine in neutral and acidic chloride solutions [15] and could be attributed to the saturation of the metallic surface with inhibitor molecules at a certain concentration.

Among the two amino acids, cysteine shows the best inhibition efficiency of the bronze corrosion in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) corrosive medium, which could be due to the presence of S in the molecular formula of this amino acid.

Electrochemical impedance spectroscopy measurements

In order to obtain further information about the kinetics of bronze corrosion in the presence of amino acids, the electrochemical process was examined by electrochemical impedance spectroscopy (EIS).

Figure 2 shows the impedance diagrams of bronze recorded at the open circuit potential after 1-hour immersion in electrolytes containing various concentrations of amino acids. The high frequency part of impedance spectra is displayed with an enlarged scale in the inserts.

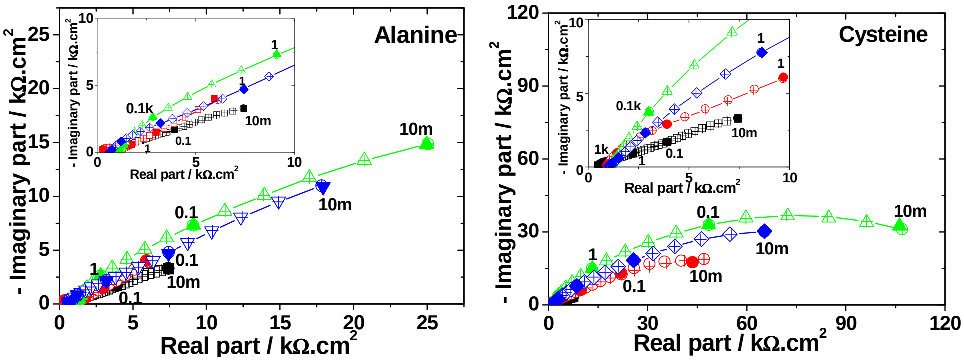

Figure 2. Nyquist plots of bronze electrode in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) solution, in the absence (□) and in the presence of different concentrations of amino acids: (○) 0.01; (Δ) 0.1; (◊) 1 mM. The symbol (—+—) corresponds to the simulated spectra. Frequencies are expressed in Hz.

It can be noticed that the impedance spectra of bronze recorded in the absence and in the presence of different concentrations of amino acids exhibit a capacitive behaviour in the whole frequency domain. The significant increase of impedance modulus in presence of the organic compounds proves the inhibition effect exerted by the two innoxious organic compounds on the bronze corrosion.

According to a.c. circuit theory [17], the impedance plots obtained for a given electrochemical system could be described by an equivalent electrical circuit involving different components (resistors, capacitors, inductors) which are associated with different phenomena from the reaction mechanism. The fitting of the experimental data to this pure electronic model allows checking the validity of the proposed mechanistic model and the calculation of the numerical values corresponding to physical and chemical phenomena involved in the electrochemical system under investigation [15].

As mentioned in a previous paper [10], although not clearly seen in Figure 2, the impedance data obtained for bronze corrosion in the absence of any inhibitors could be described by two R-C ladder circuits, which allows a suitable computer fitting of the experimental data. As a result, the (2RC) equivalent circuit from Figure 3a was adopted to carry out the non-linear regression calculation with a Simplex method.

In the presence of the amino acids, three capacitive loops, though badly separated each other are necessary for computer fitting of experimental data with an (3RC) electrical equivalent circuit (Figure 3b).

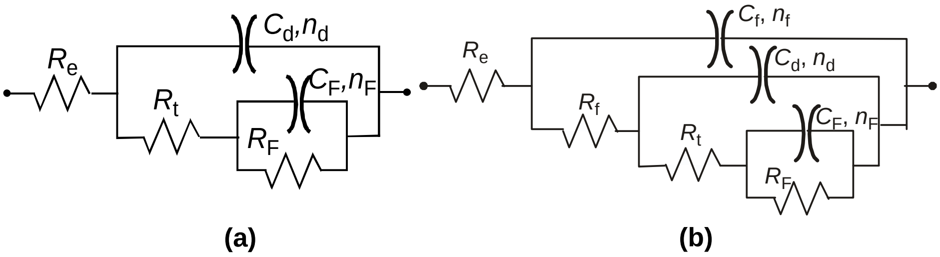

Figure 3. Equivalent electrical circuits used for computer fitting of the experimental data: (a) 2RC and (b) 3RC

In the circuits from Figure 3, R_e represents the electrolyte resistance; the *high frequency elements* (R_f and C_f) are related to the dielectric character of the corrosion products (C_f) due to formation of a thin surface layer that is reinforced in the presence of the inhibitors and by the ionic conduction through its pores (R_f); the *medium frequency contribution* (R_t and C_d) corresponds to the charge transfer resistance and to the double layer capacitance at the bronze/electrolyte interface, while the *low frequency contribution* (R_F and C_F) symbolizes the faradic resistance and faradic capacitance due to an oxidation - reduction process taking place at the electrode surface, probable involving the corrosion products. The parameters n_d, n_f, and n_F are coefficients representing the depressed characteristic of the three capacitive loops in the Nyquist diagrams.

A comparison of the experimental and calculated impedance spectra presented in Figure 2 shows that the used equivalent electrical circuits reproduce correctly the experimental results obtained in the absence and in the presence of amino acids, respectively.

The values of the impedance parameters calculated by non-linear regression of the impedance data in the absence and in the presence of different concentrations of amino acids are presented in Table 2.

Table 2. The results of non-linear regression of the impedance spectra presented in Figure 2

Inhibitors conc. (mM)	**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 (%)**
0	0.46	-	-	3.34	36.84	12.66	1652.63	16.01	-
Alanine 0.01	1.03	2.70	11.35	4.59	32.49	42.11	210.23	49.40	67.60
0.1	1.08	3.20	7.08	6.93	3.34	76.04	92.83	86.17	81.42
1	0.60	0.14	0.28	4.82	3.98	70.26	180.00	75.22	78.72
Cysteine 0.01	0.89	0.76	1.02	21.40	13.79	77.07	40.81	99.23	83.86
0.1	1.08	1.53	0.94	42.55	1.95	126.71	31.44	170.79	90.63
1	0.92	0.55	1.99	30.72	11.05	95.21	120.17	126.48	87.34

$^*R_p = R_f + R_t + R_F$

The inhibition efficiency (IE) of the amino acids was calculated from the polarization resistance values, as follows:

$$\mathrm{IE}(\%) = 100 \cdot \frac{R_p^0 - R_p}{R_p} \tag{3}$$

where R_p and R^0_p are the polarisation resistances in electrolytes with and without amino acids, respectively.

As expected, the film resistance R_f increases and attains the maximum values in the presence of 0.1 mM alanine and 0.1 mM cysteine. In the same time, the C_f values decreases proving that the surface film formed in presence of these optimum concentrations of amino acids is probably thicker and less permeable. The decreases of the R_t values observed at higher concentrations of the amino acids suggests that the surface layer formed in the presence of the inhibitors is less protective.

Furthermore, the R_t increases and C_d decrease in the presence of the amino acids as compared with the values obtained in the absence of the inhibitors. The decreases of the C_d values in the presence of the amino acids could be due to a smaller area of the electrode directly in contact with the electrolyte under the corrosion product layer or to a less conducting nature of this film. The variation of the R_F and C_F values in the presence of the corrosion inhibitors assess also the stability of the surface film.

The values of the polarisation resistance R_p, calculated as the sum (R_f + R_t + R_F) from the resistances values determined by the regression calculation (Table 2) show that the corrosion rate significantly decreases in the presence of the amino acids. This effect should be related to the inhibiting effect of the amino acids on the corrosion process, due to their adsorption on the bronze surface, forming a blocking barrier to corrosion process. The highest values of the R_p and, consequently, the maximum inhibition efficiency values were obtained in the presence of the optimal concentration of amino acids (0.1 mM alanine and 0.1 mM cysteine).

The inhibition efficiencies, calculated from ac impedance results, show the same trend as those estimated from the polarisation measurements. In the investigated experimental conditions, cysteine has proved to be the best corrosion inhibitor of bronze.

The better inhibition efficiency exhibited by cysteine compared to alanine could be explained if we take into consideration that the molecular structure of cysteine contains, apart from the amino group, a -SH group that also has a strong adsorption affinity for copper and plays an key role in the inhibition process [13, 15-16]. Consequently, cysteine can be adsorbed on the bronze surface as bidentate ligands, in which the coordination is taking place through both the amino- and mercapto- groups.

Since the corrosion process is time-dependent, the inhibiting effect exerted by the amino acids on bronze, during long-time exposure in the corrosive media was also studied.

Nyquist plots of bronze recorded after different times of immersion in the electrolytes with or without the optimum concentration of amino acids are shown in Figure 4.

By comparing the impedance spectra obtained at different immersion times in the presence of 0.1 mM alanine, it was found that the impedance increases with the immersion time up to maximum in 48 hours, and then slowly decreases with further increases of the immersion time up to 132 hours. The decrease of the inhibition efficiency at long exposure times may be due to a deterioration of the protective layer formed in the presence of alanine on the bronze surface.

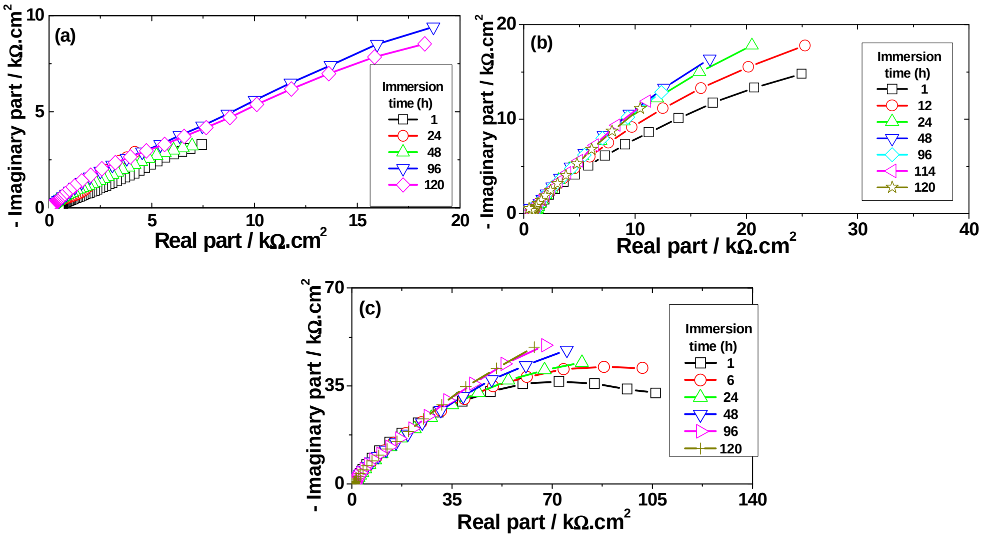

Figure 4. EIS evolution of bronze in 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$ (pH=5) solution in the absence (a) and in the presence of the optimal concentration of amino acids: (b) 0.1 mM alanine; (c) 0.1 mM cysteine.

In the presence of 0.1 mM cysteine, the impedance continuously increases and attains a maximum value in 48 hours, which tends to remain nearly constant with further increases of the immersion time up to 120 hours.

CONCLUSIONS

The electrochemical measurements showed that the investigated innoxious amino acids have fairly good inhibition properties on contemporary bronze corrosion, which makes them potential candidates for the protection of the archaeological bronzes. The investigated amino acids mainly act as cathodic inhibitors by decreasing the corrosion current and shifting the corrosion potential towards more negative values.

In the impedance diagrams, the inhibiting effect of the amino acids results in a significant increase of the impedance modulus in the whole frequency domain, and also in the appearance of the third time constant due to the formation of a protective film between the corrosion products and amino acids molecules.

In the investigated experimental conditions, disregarding its concentration in the corrosive solution, cysteine has proved to be a better inhibitor of bronze corrosion compared to alanine. The improved inhibition effect of cysteine was ascribed to the involvement of the mercapto group that allows a stronger adsorption of the organic molecule as bidentate ligands through the -SH and $-NH_2$ groups.

The variation of the impedance during long time measurements suggests that the protective effectiveness of the optimal concentrations of amino acids on bronze corrosion process is time-dependent.

The effects exerted by the two innoxious amino acids on the surface of bronze covered with artificially created patina will be presented in a future paper, giving additional data on the protectiveness action of the amino acids as corrosion inhibitors of the genuine artefacts belonging to the Bronze Age and discovered in the archaeological settlements from Transylvania.

EXPERIMENTAL SECTION

First, the composition of the non-archaeological bronze used as working electrode in the corrosion testing was selected after a preliminary investigation on the chemical composition of several authentic Bronze Age artefacts. Then, the influence of the non-toxic organic inhibitors (alanine and cysteine) on bronze corrosion in aqueous solution was investigated.

Archaeological Transylvanian bronze artefacts

The examined authentic artefacts belong to the collection of the National Union Museum at Alba Iulia, Romania. As can be seen in Figure 5, the artefacts consist in tools (sickles and scrapers) and jewellery (pendants) datable back to Late Bronze Age (XIIth century B.C.) and were discovered at Noslac – “La Manastire” (Alba County) archaeological settlement in Transylvania (Romania).

Figure 5. Examples of authentic bronze artefacts datable back to Late Bronze Age

The chemical composition of the archaeological artefacts was determined using a Quant' X ARL X-ray fluorescence spectrometer (Thermo Scientific, USA) and the results are presented in Table 3.

Table 3. Alloy composition of Transylvanian archaeological artefacts (wt-%)

Sample	**Cu**	**Sn**	**Sb**	**As**	**Zn**	**Fe**	**Pb**	**Si**	**Ni**	**Total**
S1	92.73	5.09	0.49	0.37	0.07	0.05	0.13	0.60	0.47	100
S2	88.38	9.62	0.53	0.29	0.11	-	0.08	0.61	0.38	100
S3	90.74	6.91	0.62	0.40	0.09	0.06	0.05	0.70	0.43	100
S4	90.28	7.03	0.63	0.58	0.11	-	0.15	0.75	0.47	100
S5	90.94	7.76	0.11	0.07	0.12	-	-	0.75	0.25	100
S6	87.91	9.75	0.51	0.38	0.10	-	-	0.92	0.43	100
S7	86.96	10.19	0.73	0.18	0.08	0.54	0.08	0.83	0.41	100
S8	87.82	9.59	0.83	0.52	0.08	-	0.04	0.70	0.42	100
S9	87.03	10.69	0.24	0.17	0.11	0.47	0.02	0.84	0.43	100
S10	88.12	9.61	0.48	0.35	0.09	0.25	0.11	0.63	0.44	100
S11	94.91	2.08	0.60	0.86	0.07	0.17	0.01	0.66	0.64	100
S12	86.80	9.78	0.48	0.58	-	0.06	0.08	1.62	0.60	100
S13	91.35	7.19	0.35	0.34	0.07	0.11	0.02	0.04	0.53	100

The investigated authentic Bronze Age artefacts are essentially Cu-Sn binary alloys with small amounts of Sb, As, Fe, Pb, Zn and Si as impurities (Table 3). The Sn content varies between 2.08% and 10.69%, and the mean value within the thirteen archaeological samples examined was to around 6.4%. This result justifies the choice of the modern bronze with the composition presented in Table 4 as working electrode for corrosion testing.

Table 4. Weight composition (%) of the modern bronze used as working electrode

Cu	**Sn**	**Pb**	**Zn**	**Sb**	**Ni**	**Fe**	**As**	**Si**
87.998	6.43	3.25	1.43	0.299	0.252	0.11	0.033	0.198

Reagents

The corrosive medium was an aqueous aerated solution of 0.2 g/L Na_2SO_4 + 0.2 g/L $NaHCO_3$, acidified to pH=5 by addition of dilute H_2SO_4. This electrolyte corresponds to a strong acidic rain in an urban environment.

The two amino acids (DL-alanine and DL-cysteine, Sigma Aldrich) used as corrosion inhibitors were dissolved in the electrolyte solution to the following concentrations: 0.01; 0.1 and 1 mM. The concentration ranges of the amino acids were selected taking into account the results previously reported on the study of copper corrosion in neutral and acidic solutions [13, 15-16].

The molecular structures of the investigated amino acids are shown in scheme 1.

DL - Alanine DL - Cysteine

Scheme 1. *Molecular structure of the investigated amino acids*

Electrochemical measurements

The investigation of the inhibiting properties of amino acids on bronze corrosion was performed by electrochemical methods using potentiodynamic polarisation and electrochemical impedance spectroscopy.

An electrochemical cell with a three-electrode configuration was used; the working electrode (0.38 cm^2) was made of contemporary bronze with the composition presented in Table 4; a large platinum grid and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. Prior to use, the bronze surface was mechanically polished using grit paper of 600 and 1200 and rinsed thoroughly with distilled water.

Electrochemical experiments were performed using a PAR model 2273 potentiostat controlled by a PC computer.

Anodic and cathodic polarization curves were recorded in a potential range of $E = E_{corr} \pm 200$ mV with a scan rate of 10 mV/min.

Electrochemical impedance measurements were carried out at the open circuit potential after 1-hour immersion of the bronze electrode in the corrosive solution. The impedance spectra were acquired in the frequency range 100 kHz to 10 mHz at 10 points per hertz decade with an AC voltage amplitude of ±10 mV. The impedance data were then analyzed with software based on a Simplex parameter regression.

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