



INHIBITION OF BRONZE CORROSION IN AERATED ACIDIC SOLUTION USING AMINO ACIDS AS ENVIRONMENTALLY FRIENDLY INHIBITORS

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Received July 12, 2010

The inhibiting proprieties of three innocuous amino acids, such as cysteine (Cys), alanine (Ala) and phenylalanine (PhAla) as bronze corrosion inhibitors in a strong acidic solution of 0.2 g/L Na₂SO₄ + 0.2 g/L NaHCO₃ at pH=3 was studied by electrochemical and scanning electron microscopy (SEM) techniques. Both potentiodynamic and electrochemical impedance spectroscopy (EIS) measurements revealed that these compounds have a protective effect against bronze corrosion and their inhibition efficiencies depend on the structure of amino acids. The anticorrosive efficiencies of the investigated compounds, used in their optimal concentration, decreased in the following order: 10 mM Cys (96.92 %) > 1 M Ala (80.07%) > 10 mM PhAla (52.48 %). EIS measurements also showed that the inhibitor effectiveness of the optimal concentrations of amino acids is time-dependent. SEM analysis of the corroded bronze surface confirmed that the amino acids inhibit the corrosion process, due to their ability to adsorb on the metallic surface.

INTRODUCTION

Copper and copper-based alloys are commonly used in heat exchangers, constructions, electronics, coinage, and art works etc.¹ Despite the good corrosion resistance of copper and its alloys, corrosion inhibitors have to be used in order to reduce the damage of metal dissolution in aggressive acidic media.

Typical corrosion inhibitors for copper and its alloys are heterocyclic compounds containing nitrogen, oxygen or sulphur atoms.²⁻⁶ The effectiveness of these organic molecules is based on their ability to form a protective film by several mechanisms (*i.e.* adsorption, polymerization etc.). Nevertheless, an important disadvantage of heterocyclic compounds is their toxicity and the lack of biodegradability.⁷⁻⁹ In line with the environment protection regulations and ecological policies for the use of chemicals, the latest trend in

corrosion research is focused on producing and testing new environmentally-friendly inhibitors as alternatives for the toxic substances. Recently, several works aimed to investigate the use of amino acids as corrosion inhibitors of iron,¹⁰ steel,¹¹⁻¹⁴ aluminum,¹⁵ vanadium,¹⁶ lead,¹⁷ copper¹⁸⁻²³ and its alloys²⁴ in various aggressive media. Amino acids are innocuous, biodegradable, soluble in aqueous media, relatively cheap and easy to produce at high purity.²⁵ These properties would justify the use of amino acids as corrosion inhibitors. Furthermore, in recent papers²⁶⁻²⁷ we have reported the beneficial effect exerted by several amino acids, *i.e.* cysteine (Cys), glutamic acid (Glu), methionine (Met), histidine (His), arginine (Arg) and alanine (Ala) on bronze corrosion in weak acidic electrolyte. We have found that the protection effectiveness of the amino acids on bronze corrosion strongly depends on the size and electronic effects of the substituents

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in molecule, as shown in the following sequence: Cys > Glu > Met > Arg > His. However, the efficiency of amino acids as corrosion inhibitors does not only depend on their chemical/electronic structure but also on the solution pH, because it may influence the corrosion mechanism, the state of amino acids molecules (protonated, deprotonated, zwitterion) and the state of metallic surface.²⁸

In this context, continuing our earlier work about the use of amino acids as environmentally friendly inhibitors, the aim of the present paper is to evaluate the anticorrosive properties of cysteine, alanine and phenylalanine on bronze corrosion in a strong acidic solution of 0.2 g/L Na₂SO₄+0.2 g/L NaHCO₃ at pH = 3 using electrochemical techniques, such as potentiodynamic polarization and electrochemical impedance spectroscopy measurements (EIS) was used. The surface state of bronze samples was characterized by scanning electron microscopy (SEM) coupled with X-ray energy dispersion spectroscopy (EDS).

RESULTS AND DISCUSSION

Polarisation curves

The cathodic and anodic polarisation curves were plotted separately from a potential value close to E_{corr} , after 1 hour immersion of the bronze electrode in the corrosive media, in the absence and in the presence of various concentrations of amino acids. Fig. 1 illustrates the obtained results.

In order to evaluate the corrosion parameters, the Stern-Geary relationship was applied close to the open circuit corrosion potential, where a linear behavior is expected.⁶ Consequently, the current density j near the open-circuit potential was expressed by the following equation:²⁹

$$j = j_{\text{corr}} \{ \exp(b_a (E - E_{\text{corr}})) - \exp(b_c (E - E_{\text{corr}})) \} \quad (1)$$

where b_a and b_c are the anodic and cathodic activation coefficients, respectively.

A non-linear regression calculation near zero overall current was applied to both the anodic and cathodic polarizations to calculate the kinetic parameters in the absence and in the presence of the amino acids.

The results revealed that the values of corrosion current densities determined from the two branches

are different, as was expected from Fig. 1. It is obvious that even when is applied for a short time, a polarisation in the anodic range may deeply modify the corrosion products accumulated at surface.³ Therefore, we preferred to limit our discussions to the kinetic parameters calculated from the anodic branch. The corresponding values of the corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic and cathodic activation coefficients (b_a , b_c) in the absence and in the presence of the amino acids are listed in Table 1. The inhibition efficiency (IE) was calculated using the values of the corrosion current density as described elsewhere³ and is also given in Table 1. In all cases, the values of the correlation factor R^2 varies between 0.9991 and 0.9999 indicating a good fitting result.

As it can be seen from Table 1 and Fig. 1, the corrosion potential is shifted towards the negative direction in the presence of amino acids. Moreover, the addition of the amino acids to the corrosive solution reduces the bronze corrosion rate, as attested by the decreases of the corrosion current density values. This confirms that all investigated compounds inhibit the bronze corrosion, probably due to their ability to adsorb and to form a protective layer on the metallic surface. The anticorrosive effectiveness of the amino acids on bronze is relatively weak at low concentrations. As the amino acids concentration increases, their inhibition efficiency also increases and reaches a maximum in the presence of 10 mM Cys, 1 M Ala and 10 mM PhAla. Nevertheless, in the case of Cys, a further increase of the amino acid concentration from 10 mM to 50 mM leads to a decrease of its protective efficiency. The values of Tafel coefficients in the presence of the amino acids markedly change with the inhibitors concentration, which suggests that these compounds influence the kinetics of the anodic and cathodic processes. Disregarding their concentration or molecular structure, each amino acid appears to have a more pronounced inhibiting effect on the cathodic process than on the anodic one. A possible explanation takes into account that in strong acidic media, the amino acids are protonated at the amine group and could be adsorbed on the cathodic sites of bronze, acting mainly as cathodic inhibitors.

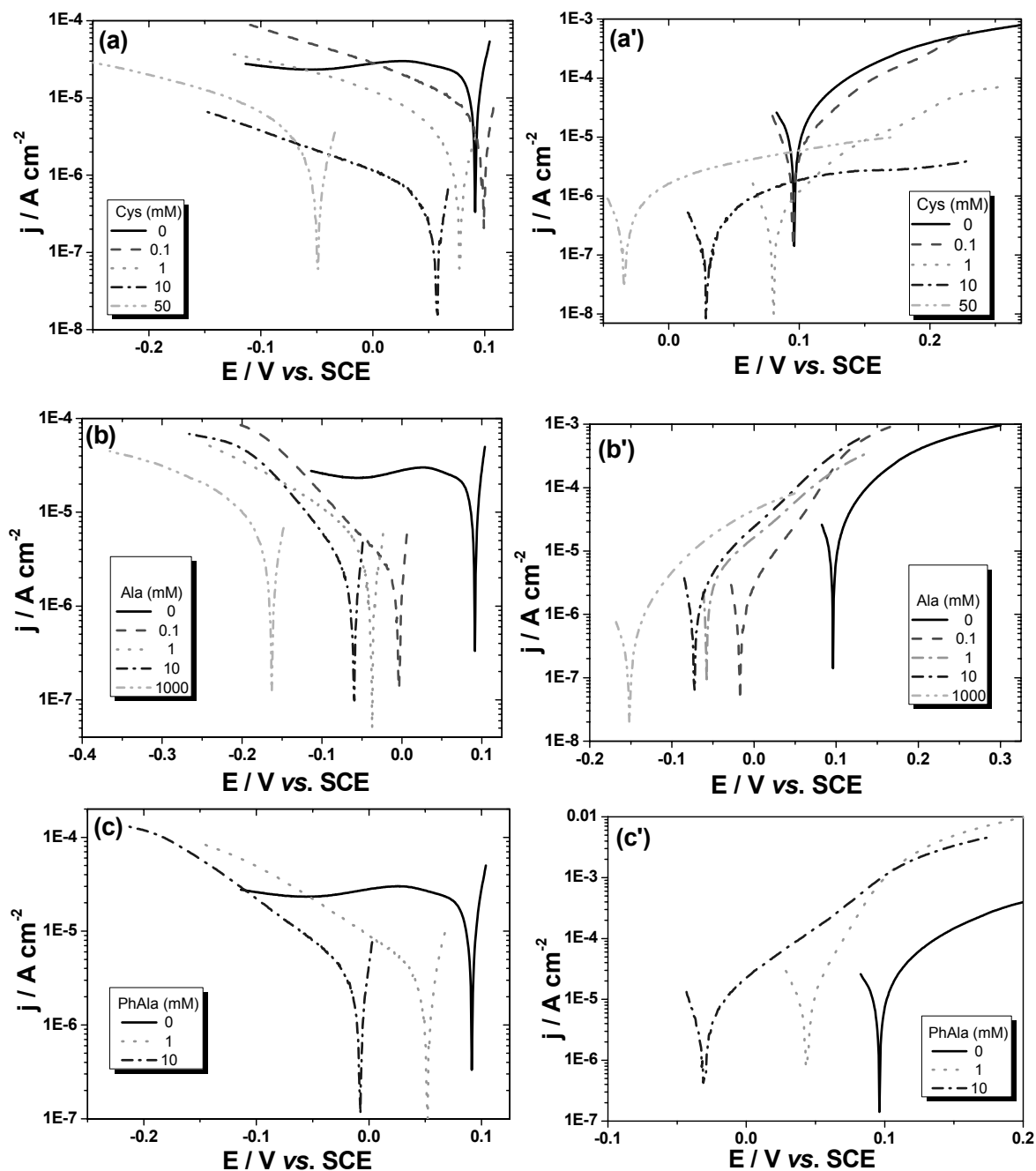


Fig. 1 – Polarisation curves for bronze in 0.2 g/L Na_2SO_4 + 0.2 g/L NaHCO_3 (pH 3) in the absence and in the presence of different concentrations of amino acids. (a – c) cathodic range; (a' – c') anodic range. Scan rate, 10 mV/min.

Table 1

Corrosion parameters for bronze in 0.2 g/L Na_2SO_4 + 0.2 g/L NaHCO_3 (pH=3) without and with the addition of amino acids, obtained by regression from the anodic potential scan data

Inhibitor conc. (mM)	E_{corr} (V vs. SCE)	j_{corr} ($\mu\text{A}/\text{cm}^2$)	b_a (V^{-1})	$-b_c$ (V^{-1})	IE (%)
0	0.097	20.00 ± 0.16	21.67 ± 0.34	12.89 ± 0.75	-
Cys	0.1	12.23 ± 0.11	41.52 ± 0.22	72.53 ± 1.52	38.85
	1	1.58 ± 0.01	41.63 ± 0.23	73.96 ± 1.50	92.10
	10	0.91 ± 0.07	13.92 ± 1.07	23.87 ± 2.27	95.45
	50	0.034	2.35 ± 0.03	14.24 ± 0.33	33.32 ± 0.82

Table 1 (continued)

Ala						
0.1		-0.016	16.37 ± 0.01	39.27 ± 0.07	62.21 ± 1.54	18.15
1		-0.057	12.79 ± 0.01	24.14 ± 0.06	69.06 ± 1.15	36.05
10		-0.072	6.47 ± 0.10	26.46 ± 0.23	28.97 ± 1.25	67.65
1000		-0.151	3.53 ± 0.001	32.55 ± 0.22	17.60 ± 0.56	82.35
PhAla						
1		0.047	13.91 ± 0.05	70.24 ± 1.35	13.34 ± 0.56	30.45
10		-0.030	8.74 ± 0.11	37.11 ± 0.23	58.20 ± 1.44	56.30

Electrochemical impedance spectroscopy measurements

Influence of the inhibitors concentration

The impedance measurements were conducted at the open-circuit potentials after 1 hour immersion in electrolytes containing various

concentrations of amino acids and the obtained Nyquist plots are shown in Fig. 2. The insets present the high frequency domain of impedance spectra in enlarged scale.

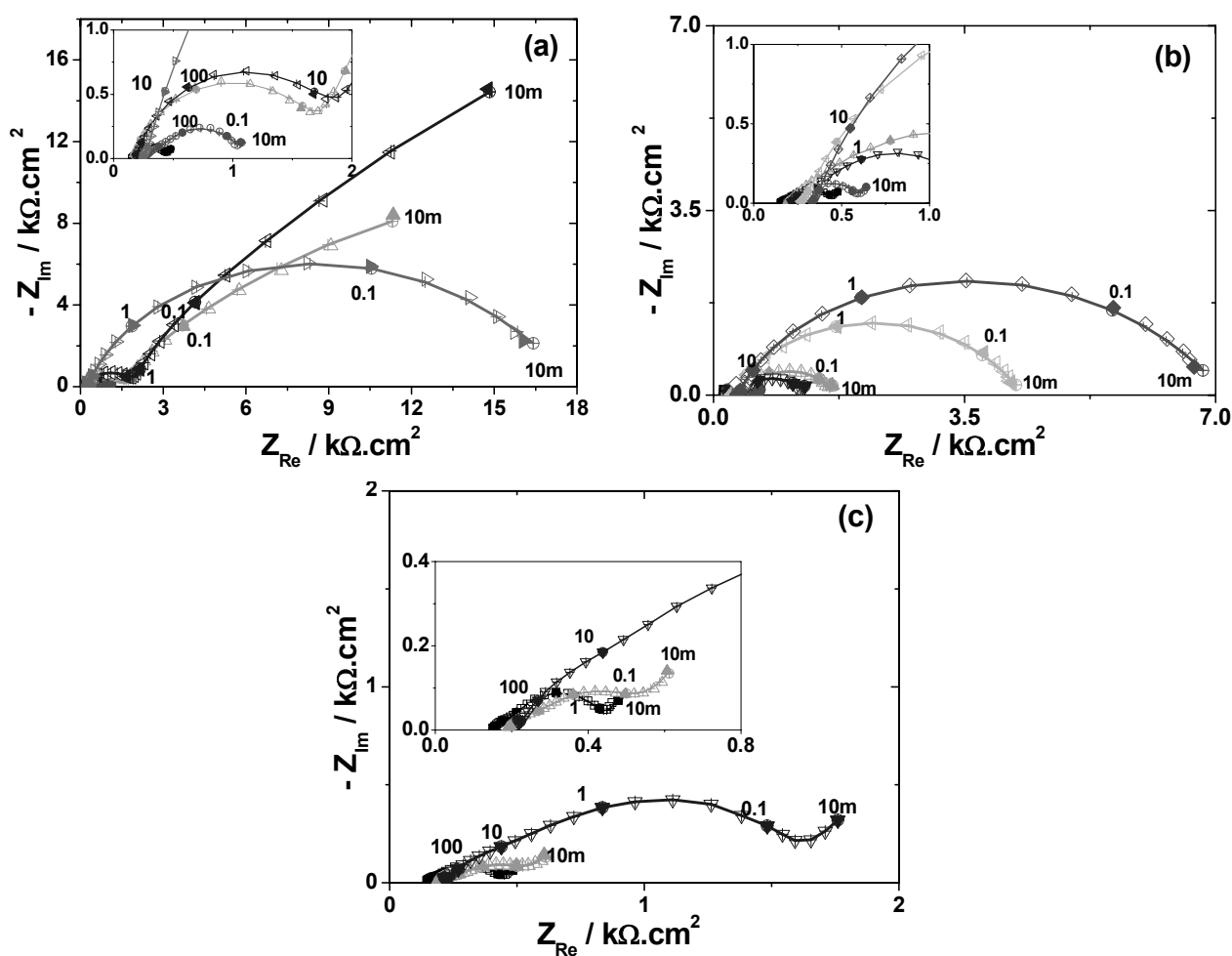


Fig. 2 – Nyquist plots of bronze electrode in 0.2 g/L Na_2SO_4 + 0.2 g/L NaHCO_3 (pH 3) solution, in the absence and in the presence of the investigated amino acids: (a) Cys; (b) Ala and (c) PhAla at different concentrations (mM): (■) 0; (●) 0.1; (▲); 1; (▼) 10; (►) 50; (◄) 500; (◆) 1000. The symbol (—+—) corresponds to the fitted data. Frequencies are expressed in Hz.

Three capacitive loops are necessary for computer fitting of experimental data obtained in the absence and in the presence of amino acids with an electrical equivalent circuit. The (3RC) electrical circuit presented in Fig. 3 was adopted to carry out a non-linear regression calculation with a Simplex method. The origin of the various

variables used in the equivalent circuit from Fig. 3 was described in a previous paper.³

The results of non-linear regression calculation with Simplex method (cross symbols) are superimposed to the experimental data in Fig. 2 and the obtained impedance parameters are given in Table 2.

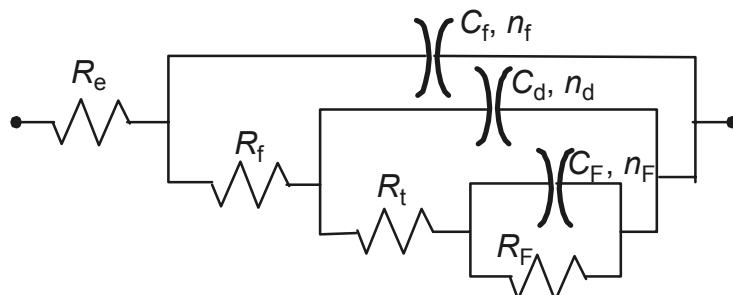


Fig. 3 – (3RC) equivalent electrical circuit used for computer fitting of the experimental data

Table 2

Parameter values for bronze corrosion calculated by non-linear regression of the impedance data using the equivalent electrical circuits from Fig. 3

Inhibitor conc. (mM)	R_e ($k\Omega\text{ cm}^2$)	R_f ($k\Omega\text{ cm}^2$)	C_f ($\mu\text{F}/\text{cm}^2$)	R_t ($k\Omega\text{ cm}^2$)	C_d ($\mu\text{F}/\text{cm}^2$)	R_F ($k\Omega\text{ cm}^2$)	C_F (mF/cm^2)	R_p^* ($k\Omega\text{ cm}^2$)	IE (%)
0	0.15	0.08	49.72	0.22	520.59	1.33	276.80	1.63	-
Cys									
0.1	0.26	0.29	69.71	0.56	389.26	3.68	192.72	4.53	6.40
1	0.16	1.65	1.74	6.55	343.38	15.14	1.37	23.34	93.01
5	0.18	1.70	1.64	9.12	306.24	26.58	0.09	37.40	95.64
10	0.18	1.79	1.42	17.01	219.12	34.09	0.07	52.89	96.92
50	0.24	0.14	9.94	11.15	16.30	5.65	3.58	16.94	90.38
Ala									
0.1	0.19	0.09	41.60	0.32	513.19	1.32	160.83	1.73	5.78
1	0.18	0.10	35.89	0.45	443.35	1.70	244.49	2.25	27.56
10	0.21	0.30	35.83	0.77	309.47	2.77	123.46	3.84	57.55
500	0.26	0.38	7.68	2.72	29.41	1.78	62.45	4.88	66.60
1000	0.33	0.41	10.55	4.81	17.95	2.96	0.27	8.18	80.07
PhAla									
1	0.19	0.13	59.54	0.26	103.23	1.72	559.50	2.11	22.75
10	0.17	0.20	54.67	0.54	346.25	2.69	80.46	3.43	52.48

$$*R_p = R_f + R_t + R_F$$

As it can be seen from Table 2, the film resistance R_f generally increases in the presence of the inhibitors, while the film capacitance decreases. These effects are enhanced by increasing the amino acids concentration. This suggests that the surface layer covering the

electrode surface in presence of the amino acids is probably thicker and more protective, which makes the ionic conduction through this layer more difficult.²⁸ The decrease of the C_d values, which results from a decrease in local dielectric constant and/or an increase in the thickness of the electrical

double layer, suggests that the amino acids act by adsorption on the metal/solution interface. The charge transfer resistance R_t increases when the inhibitors are added to solution, indicating a marked anticorrosion effect of the amino acids on bronze dissolution in strong acidic media. The value of C_F is compatible with the hypothesis on the origin of this loop attributed to an oxidation–reduction process involving corrosion products. In presence of the amino acids, R_F increases, indicating that these compounds stabilize a species covering the electrode surface.³⁰ Taking into account that the polarization resistance R_p is the parameter most closely associated to corrosion rate, the protective effectiveness of the investigated compounds will be assessed by R_p values.

The inhibiting efficiency (IE) was also calculated, using the R_p values as described in a previous paper.³ In most cases, the corrosion rate decreases in the presence of investigated amino acids and this effect is more pronounced at the highest concentration of inhibitors (Table 2). The only exception appears in the case of Cys where a decrease of the R_p value was observed at a further increase of its concentration from 10 mM to 50 mM. This phenomenon is consistent with the results obtained for other inhibitors³¹ and could be

a consequence of deterioration of the adsorbed inhibitor layer on bronze surface. In strong acidic solution, the maximum inhibition efficiency values were obtained in the presence of the optimum concentration of amino acids: 10 mM Cys, 1 M Ala and 10 mM PhAla. The inhibition efficiencies of investigated compounds calculated by EIS method show the same trend as those estimated from the polarization measurements.

As explained in previous papers,²⁶⁻²⁷ the good anticorrosive protection of Cys on bronze corrosion is probably a consequence of its adsorption on the electrode as bidentate ligand in which surface coordination is taking place through both the amino group and the –S– moiety.¹⁸ In the case of phenylalanine, the phenyl- ring could exert a steric hindrance, which probably affects the adsorption of the organic molecule on bronze surface. Therefore, the inhibition efficiency of PhAla decreases as compared to Ala.

Influence of the immersion time

Nyquist plots of bronze collected after different times of exposure in corrosive electrolytes with or without the optimum concentration of the investigated amino acids are presented in Fig. 4.

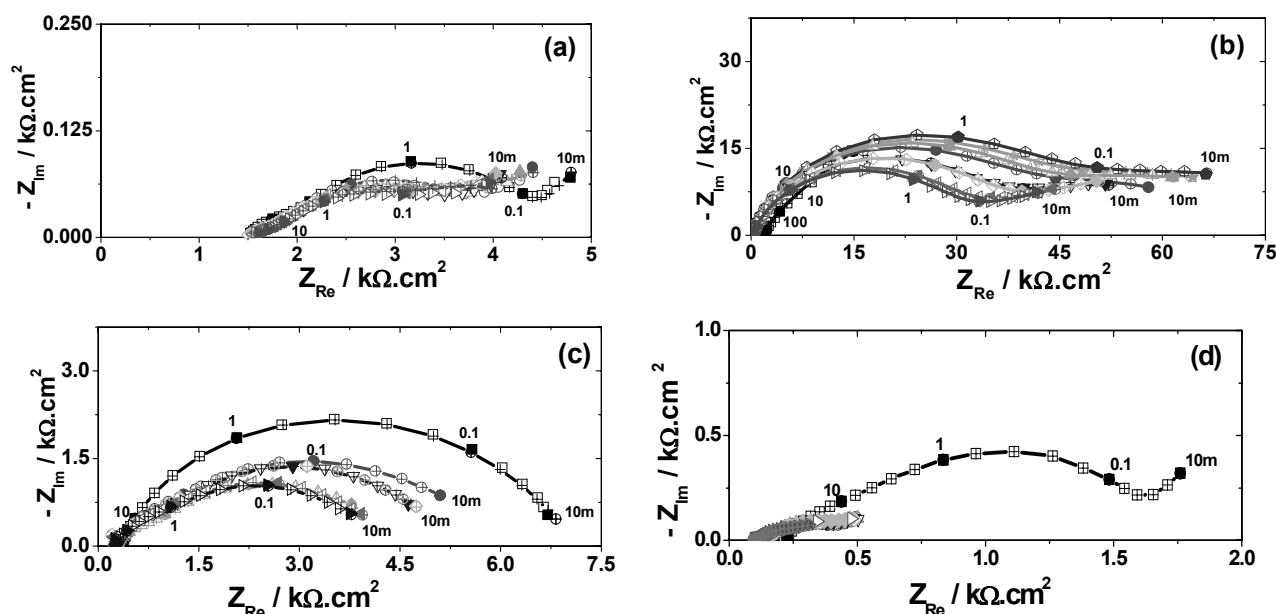


Fig. 4 – EIS evolution of bronze electrode in 0.2 g/L Na_2SO_4 + 0.2 g/L NaHCO_3 (pH 3) solution in the absence (a) and in the presence of the optimal concentration of amino acids: (b) 10 mM Cys; (c) 1 M Ala and (d) 10 mM PhAla at different immersion times (hours): (■) 1; (●) 12; (▲); 24; (▼) 36; (◆) 48; (◁) 60; (◇) 84. The symbol (—+—) corresponds to the fitted data. Frequencies are expressed in Hz.

The change of the polarisation resistance with the immersion time observed in the presence of the

amino acids proves that their protective effectiveness on bronze corrosion is time-dependent (Fig. 5).

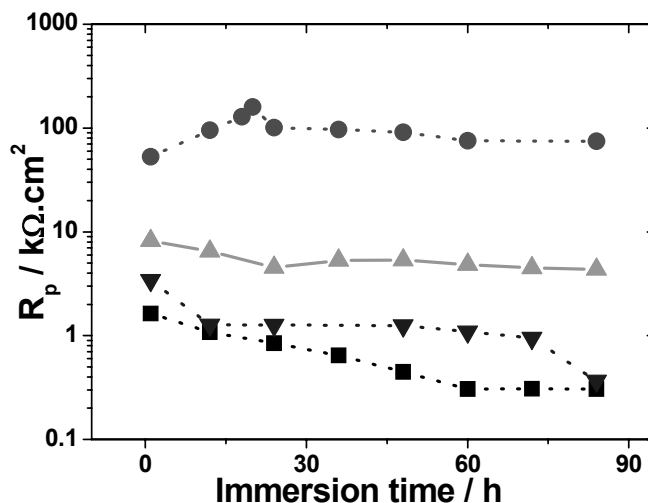


Fig. 5 – Variation of the polarisation resistance with the immersion time in the absence (■) and in the presence of the amino acids: (●) 10 mM Cys; (▲) 1 M Ala; (▼) 10 mM PhAla.

In the presence of the optimum concentration of Cys, the impedance increases with the immersion time up to the maximum in 20 hours, and then decreases with further increase of the immersion time until it reaches, after 60 hours, a value that remains almost constant. On the other hand, in the presence of the optimum concentrations of Ala and PhAla, the maximum protective effect on bronze corrosion was observed after the first hour of immersion in the electrolytes. The decrease of the inhibition efficiencies at long exposure times may be due to a deterioration of the protective layer formed in the presence of amino acids on bronze surface.

SEM-EDS analysis

Fig. 6a presents the bronze surface morphology after 66 hours of immersion in the corrosive solution in the absence of any organic compounds. It can be

seen that the bronze surface is covered with a layer of corrosion products. The slight inhibiting effect exerted by low concentrations of Cys and PhAla reduced the roughness of the bronze surface, as can be seen in Fig. 6b and 6d. In contrast, at the optimum concentration of Cys (10 mM), (Fig. 6c) almost no corrosion is visible on the metallic surface, confirming the marked inhibiting efficiency of Cys at this concentration, which is in agreement with the electrochemical results.

The EDS analysis of the bronze surface after its immersion in the corrosive solution in the presence of amino acids does not allow the identification of the organic compounds on the electrodic surface (results not shown). Nonetheless, the decrease of the double layer capacitance observed in the presence of the amino acids (Table 2) confirms their adsorption on the bronze surface.²⁴

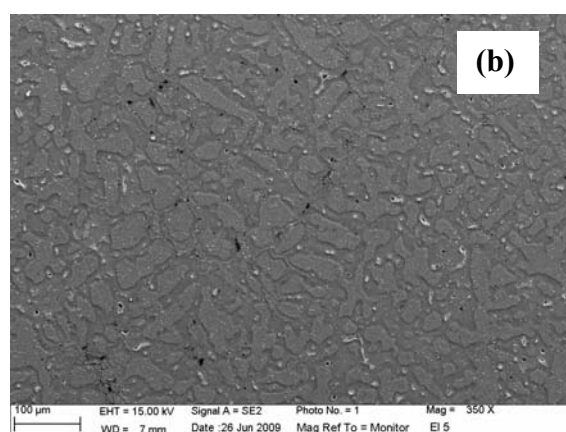
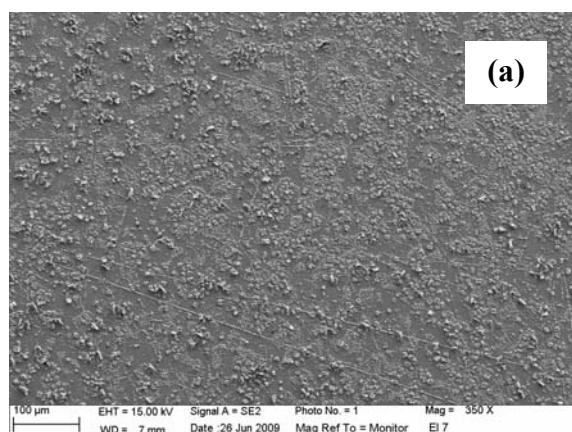


Fig. 6 – SEM micrograph of the bronze surface obtained after 66 hours immersion in 0.2 g/L NaHCO_3 + 0.2 g/L Na_2SO_4 (pH 3) in the absence (a) and in the presence of: (b) 0.1 mM Cys; (c) 10 mM Cys and (d) 1 mM PhAla.

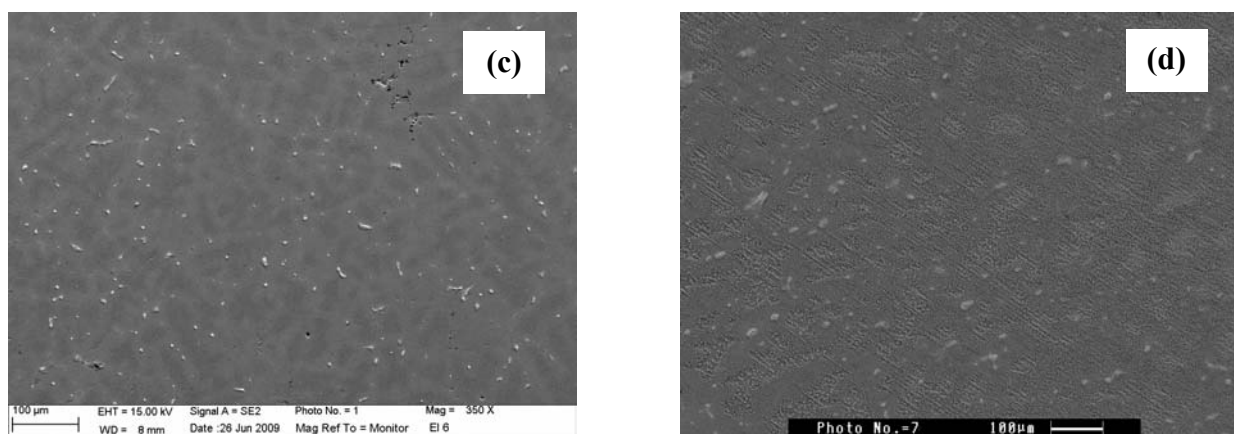


Fig. 6 – SEM micrograph of the bronze surface obtained after 66 hours immersion in 0.2 g/L NaHCO₃ + 0.2 g/L Na₂SO₄ (pH 3) in the absence (a) and in the presence of: (b) 0.1 mM Cys (c) 10 mM Cys and (d) 1 mM PhAla.

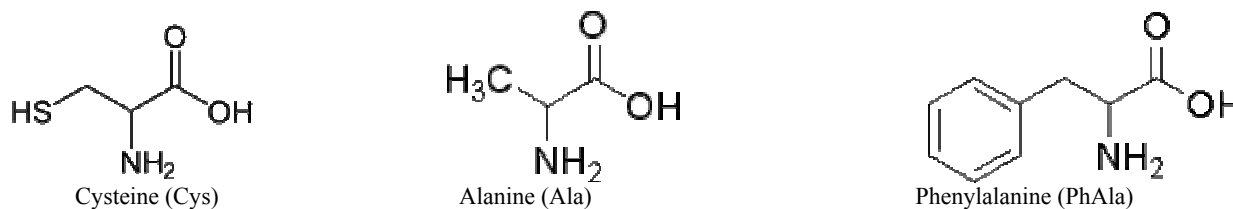
EXPERIMENTAL

The corrosive medium was an aqueous aerated solution of 0.2 g/L Na₂SO₄ + 0.2 g/L NaHCO₃, acidified to pH=3 by addition of diluted H₂SO₄. Amino acids (Sigma Aldrich, UK) were dissolved in the electrolyte solution to the concentrations range of 0.1 - 1000 mM, depending on the compounds' solubility limit. Phenylalanine presents a lower solubility in water and its highest concentration in the electrolyte was 10 mM. The molecular structures of the amino acids are shown in Scheme 1.

A three-electrode cell was used for the electrochemical experiments. The counter-electrode was a large platinum grid and a saturated calomel electrode (SCE) was used as reference

electrode. The working electrode was made of bronze ($S = 0.283 \text{ cm}^2$) with the chemical composition presented in Table 3. Prior to use, the bronze surface was mechanically polished using grit paper of 2400 and rinsed with distilled water.

Electrochemical measurements (polarization curves and EIS) were performed using a PAR model 2273 potentiostat (USA), following an experimental procedure formerly described.³ For morphological studies, the bronze surface was prepared by keeping the electrodes for 66 hours in electrolytes containing the optimum concentrations of inhibitors and observed with a Zeiss Ultra 55 SEM FEG apparatus.



Scheme 1 – Molecular structure of the investigated amino acids.

Table 3

Chemical composition (% at) of bronze working electrode

Cu	Sn	Pb	Zn	Ni	Fe	S
94.03	3.31	0.24	1.44	0.25	0.22	0.51

CONCLUSIONS

Our study reports the effects of three innocuous amino acids (cysteine, alanine and phenylalanine) on bronze corrosion in a strong acidic solution of 0.2 g/L Na₂SO₄ + 0.2 g/L NaHCO₃ at pH 3 using potentiodynamic polarization, EIS measurements and SEM-EDS investigations.

The electrochemical measurements demonstrate the inhibitive properties exerted by the investigated amino acids on bronze corrosion in strong acidic solution. Disregarding their concentration or molecular structure, each amino acid appears to have a more pronounced inhibiting effect on the oxygen cathodic reduction than on the copper dissolution process, as attested by the significant

shift of the corrosion potential towards negative values. The corrosion inhibition efficiency of the amino acids depends on their chemical structure and decreases in the following order: Cys > Ala > PhAla. In the investigated experimental conditions, the optimum concentrations of amino acids were: 10 mM Cys (96.92 %), 1 M Ala (80.07%) and 10 mM PhAla (52.48 %). Moreover, the change of the polarisation resistance with the immersion time observed in the presence of the optimal concentrations of amino acids proves that their protective effectiveness on bronze corrosion is time-dependent.

Among the investigated amino acids, cysteine was proved to be a promising environmentally safe alternative to the harmful inhibitors used for the protection of bronze against corrosion in aggressive media.

Acknowledgments: The financial support within the project PN II IDEI code 17/2009 is gratefully acknowledged. We thank S. Borensztajn (CNRS-UPR 15, Paris, France) for his help for SEM observations.

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