STUDIA UNIVERSITATIS BABEŞ-BOLYAI, CHEMIA, LII, 2, 2007

ELECTROCHEMICAL INVESTIGATION OF THE INFLUENCE OF TWO THIADIAZOLE DERIVATIVES ON THE PATINA OF AN ARCHAEOLOGICAL BRONZE ARTEFACT USING A CARBON PASTE ELECTRODE

ADRIANA VLASA*, SIMONA VARVARA, LIANA M. MUREŞAN***

ABSTRACT. The efficiency of two non-toxic thiadiazole derivatives (2-mercapto-5-R-acetylamino-1,3,4-thiadiazole and 2-mercapto-5-R-amino-1,3,4–thiadiazole) as corrosion inhibitors for bronze patina in aqueous electrolytes containing sodium sulphate and sodium hydrogen carbonate (pH 3) was studied by using a carbon paste electrode. The obtained results show the influence of the tested inhibitors on the electrochemical behaviour of patina, the strongest effect being noticed in the case of 2-amino-5-mercapto-1,3,4-thiadiazole.

Keywords: patina, bronze corrosion; corrosion inhibitor; thiadiazole derivatives, carbon paste electrode

1. INTRODUCTION

During interaction between archaeological bronze artefacts and the surrounding environment, these ancient objects became covered with a layer of corrosion products, called *patina*, whose composition strongly depends on the corrosive medium [1, 2]. Depending on the environmental conditions, the patina layer has a bluish, a green or even a brown colour, conferring to the artefacts an attractive aspect. Moreover, once formed, the patina is relative stable and acts as a protective barrier of the bronze artefact under many exposure conditions [3]. Due to these reasons and to the fact that the patina hides important archaeological information, this layer is carefully preserved on the surface of bronze artefacts. However, its stability can change under the influence of the environment and the corrosion starts

* "Babes-Bolyai" University, Department of Physical Chemistry, 11 Arany Janos St., 400028 Cluj-Napoca, ROMANIA.*E-mail: limur@chem.ubbcluj.ro

**"1 Decembrie 1918" University, Dept. of Topography, 11-13 Nicolae Iorga St., 510009 Alba Iulia, ROMANIA.

again [4]. Even archaeological bronze artefacts exposed in museum or stored in conservation room are submitted to degradation process. Therefore, in order to avoid this inconvenient, suitable treatment with coating substances are often required.

To this regard, a range of corrosion inhibitors, mainly nitrogen and sulphur-containing organic heterocyclic compounds developed for industry were tested in the conservation-restoration laboratories aiming to find a suitable corrosion inhibitor for the ancient artefacts. Among them, benzotriazole (BTA) has been widely accepted in the stabilization of copper and bronze artefacts being considered as the most efficient corrosion inhibitor over a wide temperature and pH range. However, BTA is highly toxic and its use is nowadays quite limited also because the conservation practice has proved that the stabilization of bronze artefacts with BTA is not always successful; the treatment may result in a darkening of the patina and, in some cases, in the development of a slight gloss [5].

Recently, in an attempt to characterize the effect of inhibitors on the electrochemical behaviour of patina isolated from the bronze substrate, the use of a cavity microelectrode was reported [6]. Inspired by this idea and by the possibility to avoid the influence of bronze substrate on the electrochemical response of the patina, the present work proposes the using of a carbon paste electrode for its electrochemical investigation. The influence of two non-toxic thiadiazole derivatives: 2-mercapto-5-R-acetylamino-1,3,4-thiadiazole (MAcT) and (2-mercapto-5-R-amino-1,3,4-thiadiazole (MAT) on the electrochemical behaviour of the patina scratched from the surface of an archaeological bronze artefact and incorporated in carbon paste was investigated in an electrolyte containing Na_2SO_4 and $NaHCO_3$ (pH 3) by cyclic voltammetry and polarization measurements.

The composition of patina was determined by SEM-EDS analysis.

2. EXPERIMENTAL

Materials

Experiments were carried out in an aerated solution of 0.2g/l Na_2SO_4 + 0.2g/l $NaHCO_3$, acidified to pH=3 by addition of dilute H_2SO_4.

2 mercapto-5-R-acetylamino-1,3,4-thiadiazole **(MAcT**) and 2 mercapto-5-R-amino-1,3,4 -thiadiazole (**MAT**) were synthesized in the laboratories of the Faculty of Pharmacy from Cluj-Napoca, Romania and their molecular structures are presented in figure 1.

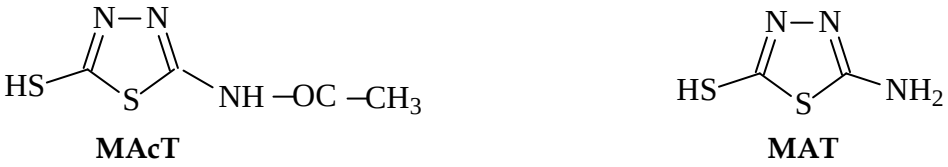

Figure 1. Molecular structure of the inhibitors

Graphite powder and paraffin oil were purchased from Fluka (Buchs, Switzerland).

All other chemicals were of analytical grade and used as received.

The investigated Transylvanian archaeological bronze artefact covered with patina layer was a pin of bronze, datable back to the Eneolithic period (around 3800 B.C.) and provided by the "1 Decembrie 1918" University of Alba-Iulia.

Preparation of carbon paste electrode

25 mg of patina gently scratched from the surface of the bronze pin were mixed with 25 mg graphite powder and 10µl paraffin oil in order to obtain the modified carbon paste electrodes. This composition was put in the cavity of a Teflon bar, forming the head of a disc electrode. Prior to all measurements, the carbon paste electrode was gently polished on paper.

Methods

In-depth composition of the metallic artefact and of the patina formed on its surface was determined by SEM-EDS analysis. A very small surface from the cross-section area of the pin was gently polished with emery paper up to the grade 1200 and finished with alumina powder. After taking SEM observation of the bronze pin (Leica model Stereoscan 440 controlled by LEO software), the composition of the artefact and of the patina was determined by EDS (Princeton Gamma-Tech, model Spirit).

Cyclic voltammetry and polarisation measurements were conducted using an electrochemical analyzer (Autolab-PGSTAT 10, EcoChemie, Utrecht, Netherlands) connected to a PC for potential control and data acquisition. The electrochemical experiments were performed in a three-electrode cell with a separate compartment for the reference electrode connected with the main compartment *via* a Luggin capillary. The working electrode was a carbon paste electrode incorporating the patina, the reference electrode was a saturated calomel electrode (SCE) and the counter electrode was a platinum foil.

3. RESULTS AND DISCUSSION

3.1 SEM and EDS measurements

The results concerning the structural and morphological characterization of the Transylvanian archaeological bronze pin covered with patina layer are presented in figure 2 and Table1.

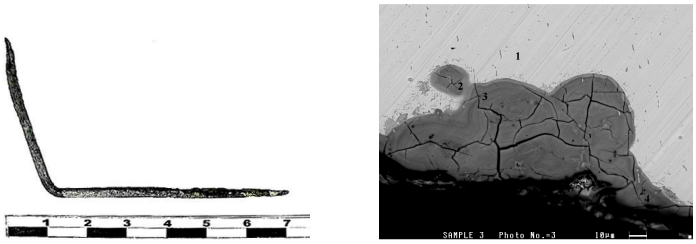

Figure 2. Bronze bended pin and SEM picture of the bronze artefact covered with a patina layer

On the points marked from 1 to 4, EDS analyses were performed, and the results are displayed in Table 1. The percents presented here were normalised with respect to the total amount of elements analysed. The carbon was not analysed quantitatively.

Table 1.

Composition of the patina layer determined by EDS in the points marked 1-4.

	Cu	Sn	Ni	Al	Fe	Cl
1	94.42	4.47	0.21	0.89	-	-
2	31.91	6.69	0.07	-	0.03	4.30
3	16.12	13.66	0.08	-	0.08	0.54
4	11.98	11.81	0.03	-	0.07	0.35

*the rest to 100% represents O

As can be observed, the investigated artefact is essentially a Cu-Sn binary alloy with a small amount of Ni as impurity. The Al detected in the EDS spectra is due to the alumina powder used for polishing a small area of the artefact.

The patina consists mainly of Cu and Sn oxides. It is interesting to note that the Sn content in patina is higher than that in bronze matrix. This phenomenon is known as "decuprification process" or a preferential dissolution of Cu [4]. The presence of Cl^- ions in the patina is due to the contact between the artefact and the soil in which it was buried during centuries.

3.2 Electrochemical measurements

The cyclic voltammograms performed with the carbon paste electrode incorporating patina in the absence and in the presence of **MAT** are presented in figure 3.

As can be observed, in the absence of additive, one anodic and one cathodic peak appear, corresponding to the oxidation/reduction of Cu/Cu^{2+} redox couple. In the presence of **MAT**, two anodic peaks were put on evidence: the peak at less positive potentials decreases with the increase of additive concentration, and the other one increases with the concentration of **MAT**. The two peaks were attributed to the dissolution of the copper deposited during the cathodic scan and to the oxidation of a complex formed between Cu(I) ions and the thiadiazole derivative, in which the thiadiazole derivatives act as bidentate ligands through the aminic nitrogen atom and the closed ring nitrogen in the complex [7]. An increase of inhibitor concentration leads to an increase of complex concentration and thus, of the second peak height and to a decrease of the first peak, due to the inhibition of copper dissolution.

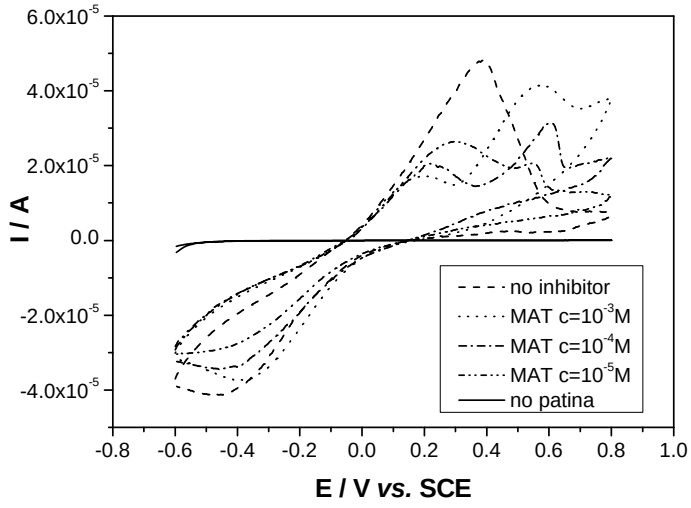

Figure 3. Cyclic voltammograms recorded in 0.2g/l Na_2SO_4 + 0.2g/l $NaHCO_3$ (pH=3) using a carbon paste electrode incorporating patina, in the absence and in the presence of **MAT**. Scan rate 0.02 V/s.

When **MAcT** is used (figure 4), two anodic peaks are observed on the voltammograms as well, their height being correlated with the concentration of the organic compound: the larger the inhibitor amount, the higher the two peak currents. However, the currents are lower than in the case of **MAT** (Table 2).

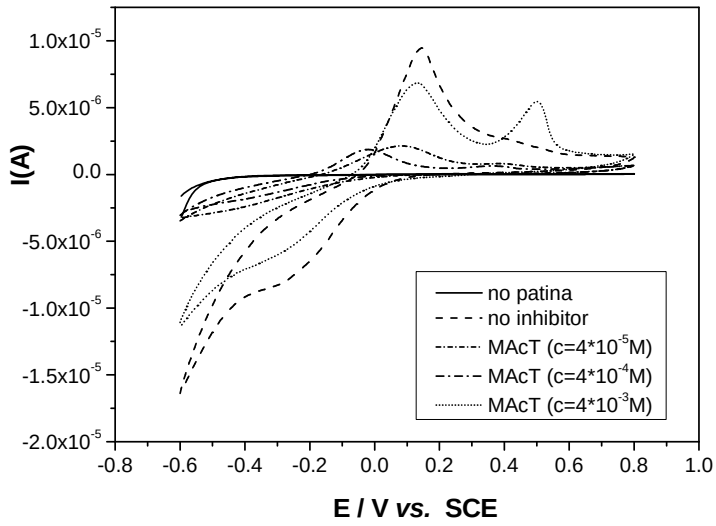

Figure 4. Cyclic voltammograms recorded in 0.2g/l Na_2SO_4 + 0.2g/l $NaHCO_3$ (pH=3) using a carbon paste electrode incorporating patina in the absence and in the presence **MAcT**. Scan rate 0.02 V/s

An explanation for this behaviour could be the depletion in electrons of the aminic nitrogen bound to the thiadiazole ring, due to the presence of the acetyl group in the molecule of **MAcT**, which leads to a poorer tendency of this compound to form a complex with Cu(I) ions. This behaviour suggests that **MAcT** has a slighter influence on the patina behaviour than **MAT**.

Table 2. Electrochemical parameters of the voltammograms recorded on the carbon paste electrode incorporating patina in the absence and in the presence of the two thiadiazole derivatives; electrolyte 0.2g/l Na_2SO_4 + 0.2g/l $NaHCO_3$ (pH=3).

Inh	Conc. (M)	$\varepsilon_{pa,1}$ (V *vs.* SCE)	$\varepsilon_{pa,2}$ (V *vs.* SCE)	ε_{pc} (V *vs.* SCE)	$I_{a,1}$ (A)	$I_{a,2}$ (A)	I_c (A)
-	0	0.385	0	0.373	$4.889 \cdot 10^{-5}$	0	$1.128 \cdot 10^{-5}$
MAT	$4 \cdot 10^{-3}$	0.146	0.554	0.324	$7.608 \cdot 10^{-6}$	$1.127 \cdot 10^{-5}$	$1.532 \cdot 10^{-5}$
MAcT	$4 \cdot 10^{-3}$	0.129	0.504	0.059	$6.148 \cdot 10^{-6}$	$3.554 \cdot 10^{-6}$	$5.202 \cdot 10^{-6}$

According to [7], the efficiency of both organic inhibitors could be associated to the extent to which they adsorb and cover the electrode surface, knowing that their adsorption depends on their structure and on the surface charge of the metal.

The polarisation curves recorded with the carbon paste electrode incorporating patina, in the absence and in the presence of the two thiadiazole derivatives in the solution are shown in figure 5.

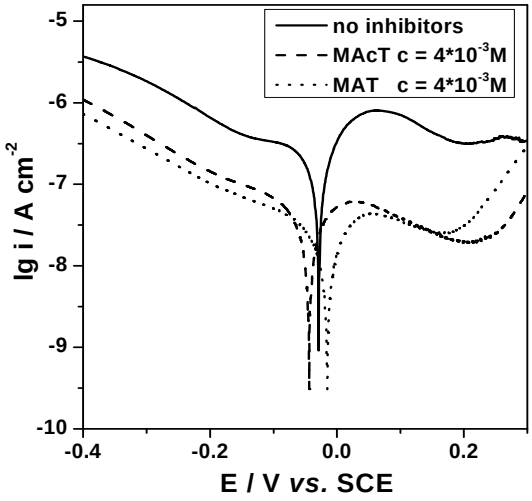

Figure 5. Influence of thiadiazole derivatives on the anodic and cathodic polarization curves of carbon paste electrode incorporating patina recorded in 0.2 g/l Na_2SO_4 + 0.2 g/l $NaHCO_3$ (pH=3). Scan rate 10 mV/min.

As can be noticed, the addition of thiadiazole derivatives gives rise to decreases of both cathodic and anodic current densities, as compared to the blank solution, in the whole applied potential range. This indicates that the investigated organic compounds inhibit the process by increasing the charge transfer resistance of the anodic dissolution of copper and acting as barriers to the diffusion of oxygen molecules from the solution to the electrode surface. Disregarding their molecular structure, the two thiadiazole derivative appears to have a more pronounced effect on the anodic process than on the cathodic one.

4. CONCLUSIONS

The new electrochemical method proposed for the study of patina originating from the surface of bronze objects, after its incorporation in carbon paste, seems to be an interesting alternative to cavity microelectrode method and can be used to characterize the effect of inhibitors on the electrochemical behaviour of the patina. Open circuit potential measurements and electrochemical impedance investigations, performed on the same experimental system, will be performed in order to obtain additional data on the inhibition mechanism of the two thiadiazoles.

The results of preliminary electrochemical investigations show that 2 mercapto-5-R-acetylamino-1, 3, 4-thiadiazole seems to have a slighter effect on the electrochemical behaviour of the patina than 2 mercapto-5-R-amino-1, 3, 4-thiadiazole in the investigated electrolyte.

ACKNOWLEDGEMENTS

The authors thank Prof. Dr. Robert Sandulescu, from "Iuliu Hatieganu" University of Medicine and Pharmacy of Cluj-Napoca for supplying us the thiadiazole derivatives, and to Prof. Dr. Iuliu Paul from "1 Decembrie 1918" University of Alba Iulia for providing the ancient bronze artefact. The financial support from EGIDE, France (Project ECO-net No. 10279NA/2005, 2006) is gratefully acknowledged.

REFERENCES

A. Kratschmer, I. O. Wallinder, C. Leygraf, Corrosion Science 44 (2002) 425-450.

B. Rosales, R. Vera, G. Moriena, Corr. Sci. 41 (1999), 625.

K. Rahmouni, *Formation et caracterisation de la patine de bronze,* Thèse de doctorat, Université Pierre et Marie Curie, Paris, 2006, Chapitre VI.

K. Rahmouni, S. Joiret, L. Robbiola, A. Srhiri, H. Takenouti, V. Vivier, Proc. Internat. Workshop „Advanced Techniques for Energy Sources Investigation and Testing", 4-9 Sept. 2004, Sofia, Bulgaria, P8-1.

L. Robbiola, J.M. Blengino, C. Fiaud, Corr. Sci. 40 (12), (1998), 2083.

L. Ying, F. Haitao, Z. Yifan, W. Wuji, J. Mat. Sci., 38 (2003) 407.

R. Faltenmeier, SSCR Journal 9, (1998), 1.