

## A STUDY ON THE CORROSION RESISTANCE OF BRONZES COVERED WITH ARTIFICIAL PATINA

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### *Abstract*

*In recent years, due to increased air pollution, bronze objects exposed in urban areas suffer continuous degradation. Therefore, it is important to find efficient methods to protect them against corrosion. The present work aims to investigate the corrosion resistance of various artificial patina currently used in bronze sculpture. Once formed, the patina is relative stable and acts as a protective coating of the bronze object under many exposure conditions. The protective effect of different artificial patinas was comparatively investigated by electrochemical and non-electrochemical methods.*

*Keywords: bronze; corrosion; patina; polarization curves.*

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### **Introduction**

A bronze surface exposed to the atmosphere forms a thin layer of corrosion products and that layer, formed naturally is called noble patina [1 - 5]. The final quality of the patina varies depending on the composition of the alloy and the environmental conditions it develops in. From a chemical point of view that layer can be described as a hydrated copper oxide stabilized on a copper oxide substrate [1, 6 - 8].

Many factors influence the initial development of the patina, some of them may be active throughout the life of a work of art. The surface and the color of a work of art show evidence of prolonged contact with pollutants in the atmosphere. The most damaging are chlorides (sodium chloride, which allows the development of copper chloride), sulfates and oxides, especially sulfur dioxide [8 - 12].

A common method to protect bronze surfaces is to cover them with an artificial patina, by using chemical reagents or by electrochemical methods [13 - 14]. Artificial patinas offers surface protection against corrosion and it also has an aesthetic value.

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The first evidence of the use of artificial patina dates back to antiquity. Mirrors dating from the Bronze Age were discovered in China which indicated that there are chemicals deliberately placed on the surface of bronze [15].

That shows that from ancient times artists wanted that the works of art made by them be durable and have outstanding aesthetic properties. Therefore, finding artificial patinas to protect works of art made of bronze is a current concern.

The main objective of this paper is to study the protective effect of various artificial patinas deliberately produced by sculptors on bronze. The study was conducted under conditions that simulate acid rain.

## Experimental

To conduct the electrochemical studies, a contemporary bronze object was selected, whose chemical composition, displayed in Table 1, is close to the bronze used by sculptors in the early 20<sup>th</sup> century

**Table 1.** The chemical composition of the used alloy

Alloy	Cu [%]	Sn [%]	Impurities, [%] max										
			Zn	Pb	Sb	Fe	Al	S	Bi	Mg	As	Mn	Ni
CuSn8	rest	7-9	0,8	1,0	0,1	0,2	0,02	0,1	0,01	0,01	0,15	0,2	1,0

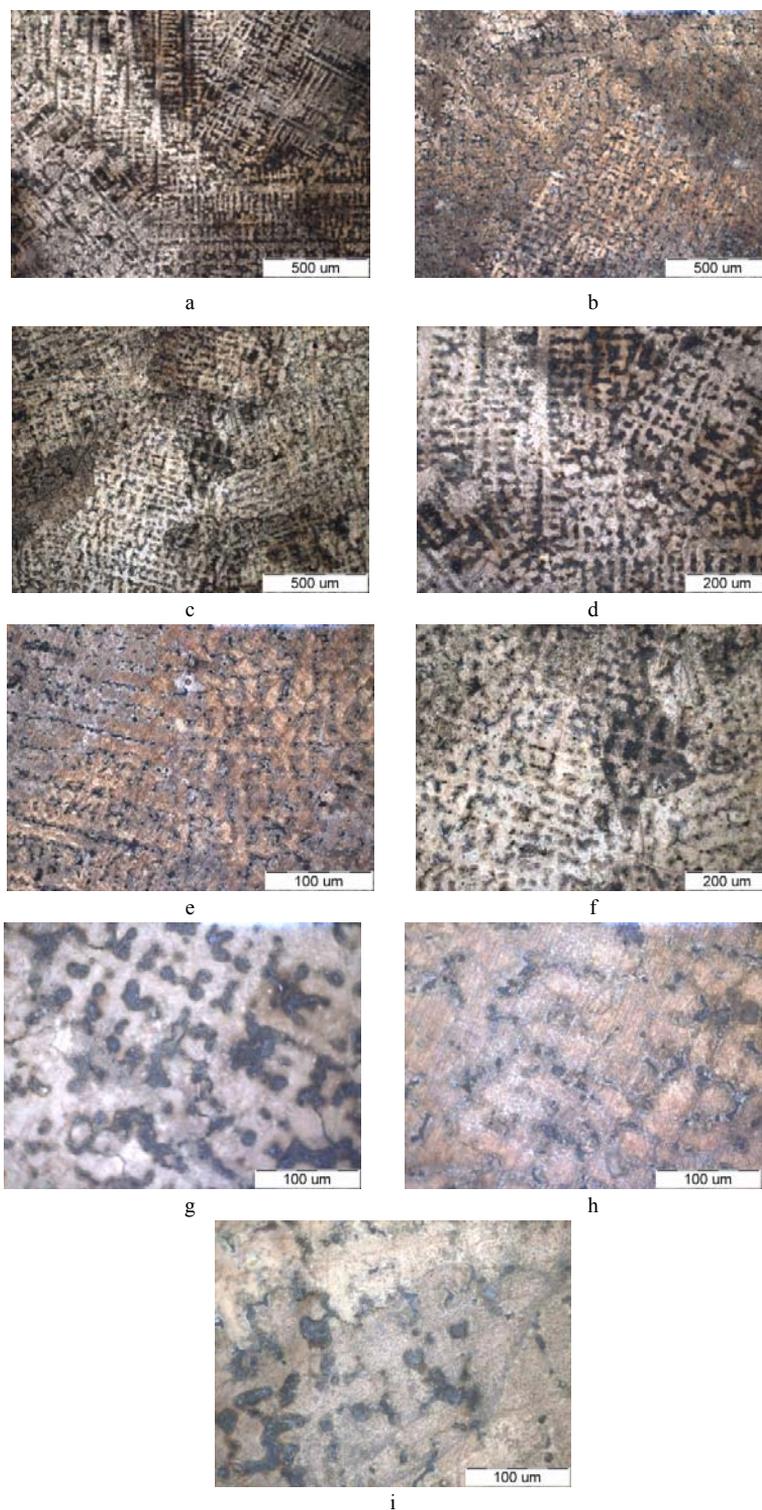
Figure 1 presents the microscopic structures of electrodes, magnified at 100X, 200X, 500X, which were subjected to accelerated corrosion in an environment that simulated acid rain.

For the microscopic study the electrodes were polished on the sample polishing machine with alumina paste, after which the surface was washed with ammonia cupric chloride. The study of the surface was done by optical microscopy (OLIMPUS GS 51).

The images in Figure 1 display the dendritic segregation of the  $\alpha$  solid solution and interdendritic segregations of eutectoid  $\alpha + \delta$  in small quantities. The eutectoid  $\alpha + \delta$  is formed in a Cu - Sn alloy and results from the decomposition of phase  $\gamma$  at a temperature of 520°C (see the equilibrium diagram Cu - Sn). According to the picture displayed in the Metallurgic Atlas, the structure is the one specific for cast bronze.

The electrochemical measurements were performed on a PC – controlled electrochemical analyzer AUTOLAB – PGSTAT 10 (Eco Chemie BV, Utrecht, The Netherlands) using a three electrodes cell containing a working electrode, a saturated calomel electrode (ECS) as reference electrode and a platinum counter electrode.

The working electrodes made of bronze CuSn8, cylindrical, were placed in a PVC tube, while the sealing was assured with epoxy resin.



**Fig. 1.** Microscopic structure of bronze used for electrochemical studies:  
a,b,c – 100X; d,e,f – 200X; g,h,i– 500X

Thus, the surface of the electrode exposed to the solution was circular, with a surface  $S = 1,76 \text{ cm}^2$ . For the electrical contact a metal rod was attached (Fig. 2).



Fig. 2. The electrodes used during the experiments

The electrolyte solution for corrosion measurements containing  $0.2 \text{ g/L Na}_2\text{SO}_4 + 0.2 \text{ g/L NaHCO}_3$  ( $\text{pH} = 5$ ).

The study was conducted on three electrodes. The electrodes were covered with an artificial patina: electrode (1) was treated with flowers of sulphur, electrode (2) was treated with a solution containing iron ions and nitric acid and electrode (3), with iron ions and copper sulfate

### Results and discussion

The experiments started by measuring the potential of the working electrode in an open circuit for a period of 3600 seconds, the records being presented in Figure 3.

As shown in the figure 3, for all studied electrodes, in the first minutes of immersion in the corrosive solution, the potential in open circuit evolves towards more positive values, reaching a stationary value after approx. 35 minutes.

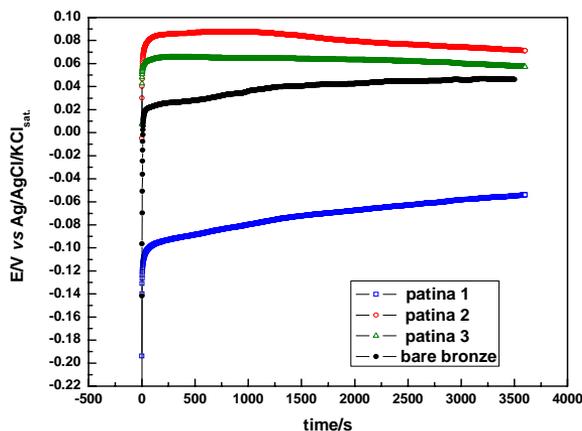


Fig.3. Time variations of the open circuit potential of the bronze electrodes immersed in  $0.2 \text{ g/L Na}_2\text{SO}_4 + 0.2 \text{ g/L NaHCO}_3$  ( $\text{pH} = 5$ )

This behavior can be attributed to the chemisorptions of oxygen on the surface of the dissolved bronze, along with the formation of surface oxide layers, hydrosulphate and/or hydroxycarbonate [17].

It can be noticed that the open circuit potentials of the coated electrodes (2) and (3) are more positive than that of bare bronze, suggesting an interaction of the patina with the anodic process (metal dissolution), while the open circuit potential of electrode (1) is more negative than that of uncovered bronze, suggesting a possible interaction with the cathodic process (reduction of O<sub>2</sub>).

To determine the polarization resistance of the electrodes, linear polarization curves were recorded, in the potential domain of ± 20 mV around the value of the open circuit potential (ocp) (Fig. 4). The polarization resistance values for each electrode, calculated as the inverse of the slope of each curve, are shown in Table 2.

The highest value for R<sub>p</sub> was observed in the case of the electrode (2), treated with a solution containing iron ions and nitric acid.

To determine the kinetic parameters of the corrosion process, polarization curves were recorded in the potential range of ± 200 mV vs. ocp (Fig. 5).

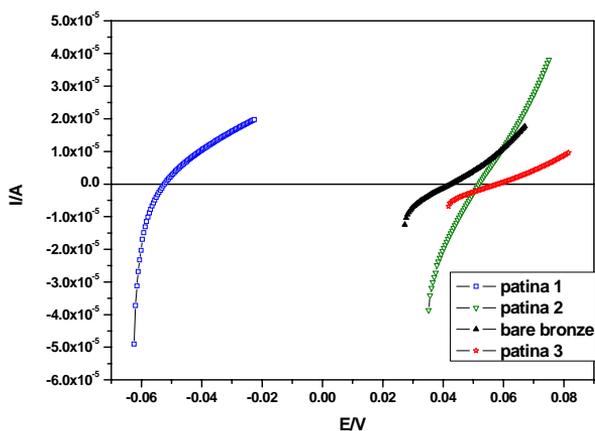


Fig. 4. Linear polarization curves (± 20 mV vs. ocp) for the studied electrodes immersed in 0.2 g/L Na<sub>2</sub>SO<sub>4</sub> + 0.2 g/L NaHCO<sub>3</sub> (pH = 5)

Table 2. The value of polarization resistance (R<sub>p</sub> = 1/p, p is the slope of the curve)

Electrode	Slope (p)	R <sub>p</sub> =1/p [Ω]
Patina 1	7,25x10 <sup>-4</sup>	1380
Patina 2	3,29x10 <sup>-4</sup>	3040
Patina 3	8,19x10 <sup>-4</sup>	1220
Bare bronze	3,24x10 <sup>-4</sup>	2060

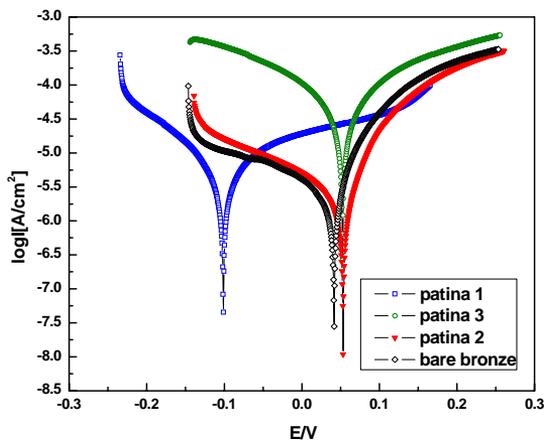


Fig. 5. The polarization curves ( $\pm 200$  mV vs. ocp) for the studied electrodes immersed in 0.2 g/L  $\text{Na}_2\text{SO}_4$  + 0.2 g/L  $\text{NaHCO}_3$  (pH = 5)

The kinetic parameters of the corrosion process were determined from the Tafel interpretation of the polarization curves and the results are presented in Table 3.

Table 3. Corrosion process parameters for the examined samples

Electrode	Ocp [mV]	E <sub>cor</sub> [mV]	i <sub>cor</sub> [ $\mu\text{A}/\text{cm}^2$ ]	$\beta_a$ [mV]	$\beta_c$ [mV]
Patina 1	-48	-101	3,25	91	77
Patina 2	62	53	2,93	43	105
Patina 3	56	53	50,75	159	178
Bare bronze	51	46	5,362	46	284

As shown in Table 3, the coated electrode 3 is the less resistant to corrosion and it presents accelerated corrosion in comparison with bare bronze. Treatment 2 seems to be the best among the treatments tested. However, the amelioration of the corrosion rate is not significant. That is due to the fact that the patina layer is not continuous, as can be seen in Figure 6.



Fig.6. The electrode surfaces after the corrosion test in a solution containing 0.2 g/L  $\text{Na}_2\text{SO}_4$  + 0.2 g/L  $\text{NaHCO}_3$  (pH = 5).

## Conclusions

Accelerated corrosion tests in an environment that simulated acid rain on contemporary bronze covered with different artificial patinas, revealed that the investigated patinas have a limited protection effect on bronze corrosion. The differences between their corrosion rate and that of uncovered bronze are not important because the patina layers were not enough compact and uniform.

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## References

- [1] R. Picciochi, A.C. Ramos, M.H. Mendonça, I.T.E. Fonseca, *Influence of the environment on the atmospheric corrosion of bronze*, **Journal of Applied Electrochemistry**, **34**, 2004, pp. 989-995.
- [2] L. Robbiola, J.M. Blengino, C. Fiaud, *Morphology and mechanisms of formation of natural patinas on archaeological Cu - Sn alloys*, **Corrosion Science**, **40**, 1998, pp. 2083-2111.
- [3] L. Robbiola, R. Portier, *A global approach to the authentication of ancient bronzes based on the characterization of the alloy - patina - environment system*, **Journal of Cultural Heritage**, **7**, 2006, pp. 1-12.
- [4] K.P. FitzGerald, J. Nairn, G. Skennerton, A. Atrens, *Atmospheric corrosion of copper and the colour, structure and composition of natural patinas on copper*, **Corrosion Science**, **48**, 2006, pp. 2480-2509.
- [5] F.J.R. de Oliveira, D.C.B. Lago, L.F. Senna, L.R.M. de Miranda, E. d'Elia, *Study of patina formation on bronze specimens*, **Materials Chemistry and Physics**, **115**, 2009, pp. 761-770.
- [6] C. Chiavari, A. Colledan, A. Frignani, G. Brunoro, *Corrosion evaluation of traditional and new bronzes for artistic castings*, **Materials Chemistry and Physics**, **95**, 2006, pp. 252-259.
- [7] G.M. Ingo, T. de Caro, C. Riccucci, S. Khosroff, *Uncommon corrosion phenomena of archaeological bronze alloys*, **Applied Physics A, Material Science & Processing**, **83**, 2006, pp.581-588.
- [8] A. Domenic-Carbo, M.T. Domenic-Carbo, I. Martinez-Lazaro, *Electrochemical identification of corrosion products in archaeological artefacts. A case study*, **Microchimica Acta**, **162**, 2007, pp. 351-359.
- [9] J.D. Chelaru, V.F. Soporan, O. Nemeş, *Time analysis of King Matthias The I Sculptural Group*, **International Journal of Conservation Science**, **1**, 2010, pp. 69-74..
- [10] M.P. Casaletto, G.M. Ingo, M. Albin, A. Lapenna, I. Pierige, C. Riccucci, F. Faraldi, *An integrated analytical characterization of corrosion products on ornamental objects from the necropolis of Colle Badetta-Tortoreto (Teramo, Italy)*, **Applied Physics A: Materials Science & Processing**, **100**, 2010, pp. 801-808.

- [11] I. Sandu, A. Dima, I.-G. Sandu, **Restauration and Conservation of Metal Objects**, Corson Publishing House, Iași, 2002.
- [12] I. Sandu, **Deterioration and Degradation of the Cultural Patrimony Treasures**. vol. I. Supply of Inorganic Materials, „Alexandru Ioan Cuza” University Publishing House, Iași, 2008.
- [13] L. Mureșan, S. Varvara, E. Stupnišek-Lisac, H. Otmačić, K. Marušić, H. Takenouti, *Protection of bronze covered with patina by innocuous organic substances*, **Electrochimica Acta**, **52**, 2007, pp. 7770-7779.
- [14] A. Vlăsa, S. Varvara, L. Mureșan, *Electrochemical investigation of the influence of two thiadiazole derivatives on the patina of an archaeological bronze artefact using a carbon paste electrode*, **Studia Universitatis “Babeș – Bolyai”**, **2**, 2007, pp. 63-71.
- [15] P. Kipper, **Patina for Silicon Bronze**, Regal Printing, Hong Kong, 2003.
- [16] J.D. Chelaru, V.F. Soporán, O. Nemes, T. Koloszi, V. Duca, *The influence of the environmental factors on the King Matthias Sculptural Group*, **International Conference 16th Building Services, Mechanical and Building Industry Days**, 2010, pp. 265-272.
- [17] N. Souissi, L. Bousselmi, S. Khosrof, E. Triki, *Electrochemical behavior of an archaeological bronze alloy in various aqueous media: New method for understanding artifacts preservation*, **Material and Corrosion**, **54**, 2003, pp. 318-325.
- [18] T. Koloszi, A. Pasat, R. Moraru, O.M. Gui, J.D. Chelaru, *Digital techniques in reinforcement and conservation of a large sculptural group. Case study: the sculptural group of Mathias I in Cluj Napoca, Romania*, **5<sup>th</sup> International Conference on Interdisciplinarity in Education - ICIE'10**, Tallinn, Estonia, 2010.

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