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Composition and electrochemical properties of natural patinas of outdoor bronze monuments

C. Chiavari[a,*], K. Rahmouni[b], H. Takenouti[b,1], S. Joiret[b], P. Vermaut[c], L. Robbiola[d,**]

[a] *Dipartimento di Scienza dei Metalli, Elettrochimica e Tecniche Chimiche, Università di Bologna, Via Risorgimento 4, It-40136 Bologna, Italy*
[b] *LISE, CNRS, Case 133, Université Paris 6, 4, place Jussieu, F-75252 Paris Cedex 05, France*
[c] *Groupe de Métallurgie Structurale, UMR 7045 CNRS, ENSCP, Université Paris 6, 11 rue P&M Curie, F-75231 Paris Cedex 05, France*
[d] *Laboratoire d'Electrochimie et de Chimie Analytique, UMR 7575 CNRS, ENSCP, Université Paris 6, 11 rue P&M Curie, F-75231 Paris Cedex 05, France*

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Abstract

The present study concerns the chemical–physical and electrochemical characterizations of the corrosion compounds formed on outdoor bronzes exposed in urban conditions. Here, we focused on the pale green patinas of surfaces directly exposed to the rainfall leaching. The investigation has been performed from scraped-off patina products of a well representative outdoor bronze monument (Monument to Francis Garnier, 1898) situated in Paris (France). The composition of the patina was analysed by energy dispersive spectrometry (EDS), coupled with SEM, and Raman spectroscopy. Structural characterization was conducted through high-resolution TEM (EDS coupled). The electrochemical reactivity of patina was investigated by cyclic voltammetry and EIS with a microcavity electrode in sulphate solution at pH 2 and 5.6 with time of immersion (up to 10 h). The bronze patina corresponds to a two-layer structure. The external layer is characterised by a marked selective dissolution of Cu and Zn of the alloy, which has been determined from the calculation of dissolution factors. The same phenomenon with the same amplitude has been evidenced on other bronze monuments used for comparison. The pale green patina is a complex mixture of crystalline copper hydroxisulphate and of amorphous/nanocrystal Sn-containing compounds. This patina is stable at pH 5.6 and reactive at pH 2 in relation with the dissolution of copper sulphate compounds in the acidic solution.

Keywords: Quaternary bronze; Selective dissolution; Cavity microelectrode; Structural characterization; HR-TEM

1. Introduction

Outdoor bronzes (Cu–Sn–Zn–Pb alloys) spontaneously form corrosion layers, usually called patinas, producing a relative protective effect to the substrate metal. Nevertheless since the last decades, the increase of rain acidity induced a strong modification of the nature and properties of the patinas. In urban atmosphere, the present patinas are unstable. As for evidence, the green traces of copper salts very often observed on basements of outdoor monuments are the results of an important leaching of bronze surfaces directly exposed to rainfalls. Numerous investigations have been conducted to understand the corrosion processes and patinas formation on copper and bronze [1–15]. It has often been assumed that bronze corrosion in atmosphere reacts similarly as for pure copper one. However, alloying elements induce specific behaviour of bronze which differs from pure copper [6,8,9,13,15]. A general framework for the understanding of the corrosion processes of bronzes in outdoor condition has been proposed [14,15] taken into account the composition of the corrosion products with exposure conditions. It has also been evidenced that for surfaces directly submitted to rainfalls, a cyclic process of corrosion is engaged. The combined action of chemical dissolution and leaching inexorably conducts to an important loss of bronze thickness with time [14]. More recently, experiments have been performed on bronzes exposed in corrosive media (e.g., simulated rainwater [8,9], aqueous sulphate or chloride solutions [10–13]) in order to simulate natural patinas. The composition and the electrochemical characterization of these artificial patinas revealed that both copper-rich and tin-rich containing compounds are present and may play an

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[*] Corresponding author.
[**] Corresponding author. Tel.: +33 1 44 27 67 09; fax: +33 1 44 27 67 10.
E-mail addresses: chiavari@bomet.fci.unibo.it (C. Chiavari), luc-robbiola@enscp.fr (L. Robbiola).
[1] ISE member.

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active role in the protection of bronze with or without inhibitive treatments.

However, even if clear progresses have been reached according to restoration–conservation objectives, the exact nature and electrochemical properties of the patina compounds formed on bronze monuments in atmospheric conditions remain still undetermined. Thus, it is of prime importance to fulfil this lack of knowledge for a better understanding of patina formation and also to validate if the artificial patinas obtained in laboratory are representative enough of patinas formed in natural conditions.

The present study concerns the chemical–physical and electrochemical characterizations of the corrosion compounds of pale green patinas, formed on the surface directly exposed to leaching. The investigation has been performed on the corrosion products scraped-off from a selected bronze monument situated in Paris. The patina has been mechanically sampled from the outermost surface up to the alloy according to the stratigraphy of the corrosion layers. The samples were analysed following a methodology considering, on the one side, the compositional and structural characterization of the patina and, on the other side, the electrochemical properties. The composition was determined by energy dispersive spectrometry (EDS) coupled with SEM and Raman spectroscopy. The structure was investigated through high-resolution TEM (EDS coupled). The electrochemical reactivity of patina was analysed by cyclic voltammetry (CV) and electrochemical impedance spectrometry (EIS) with a cavity microelectrode in aqueous sulphate solution.

2. Experimental conditions

2.1. Materials

The outdoor bronze selected for this study was the monumental group shown in Fig. 1, representing the funeral tombstone of Francis Garnier, whose casting dates from 1898. The statue is well representative of the problem we are concerned as located in a traffic area of Paris, in the centre of a crossroad, and fully exposed to the urban polluted atmosphere.

Actually, by in situ visual observation, several signs of the destabilisation of the patina were present. Although the structure of the monument looked stable, the external surface was fully and extensively corroded. The bronze surface showed different morphologies of decay as usually observed for outdoor monuments [14,15]. In particular, different zones of interest could be noticed: (i) fully exposed areas, with evident signs of rainfall leaching, corresponding to porous and powdery pale green products; (ii) partially or completely sheltered areas with a black opaque surface (thick deposit of black crusts and corrosion products). Finally, there was evidence of infiltrations of leached green corrosion products through the joints of the granite basement, up to the sidewalk, clearly evidencing the solubility of the current patina.

In this work we focused on pale green surfaces exposed to rainfalls. After a global visual examination of the monuments, the patina corresponding to these areas was sampled (Fig. 2).

The specimens were mechanically scraped off throughout all the depth of the patina, in order to obtain a stratigraphy, from the very external layer (pale green—FG-1 and FG-2 samples) up to the internal layer (red-brown—FG-3 and FG-4 samples) and the alloy (FG-5). From the sampling, the external pale green layer was found markedly thicker (200–500 μm) than the internal layer.

Fig. 1. Monument to Francis Garnier, Paris—front part exposed to the North.

Fig. 2. Detail of the investigated area of the Monument to Francis Garnier (North part). The dashed circle presents the investigated area.