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Case study

Investigation of a naturally patinated bronze artifact originating from the outdoor statuary group of Mathias Rex

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ABSTRACT

The present work aims to investigate the morphology and composition of natural patina formed after long-term atmospheric exposure (∼100 years) on the bronze screws used in assembling the statuary group of Mathias Rex, placed in the center of Cluj-Napoca, Romania. The chemical composition of the bronze and of the natural patina, formed on the screws' surface were determined by X-ray fluorescence analysis, and the morphology of the latter was determined by SEM - EDX cartographies.

1. Introduction

Outdoor bronze sculptures are highly susceptible to corrosion in many environments. Depending on the environmental conditions, bronzes became covered with a layer of corrosion products, called patina, which has a composition that strongly depends on the corrosive medium [1].

The recent restoration of the bronze statue of Mathias Rex, placed in the center of Cluj-Napoca, Romania (Fig. 1), which was cast in 1902, provided a unique resource for assessing the impact of environmental conditions on the degradation of a monumental bronze and to investigate the natural patina covering the bronze pieces, which had to be replaced. The statuary monument's total height is of 12.67 m. The pedestal of the sculptural group (6.37 m tall) was designed to carry the weight of 16 tons of bronze representing an equestrian statue reaching 6.30 m. Besides Mathias Rex, there are also four bronze characters positioned on the pedestal platform. All of them are made of bronze on metallic frame and the different pieces were assembled by using bronze or steel screws.

The King Matthias statuary group was exposed outdoors under atmospheric corrosion and, because of increasing pollution in recent years the monument was subjected to an acceleration of corrosion and depreciation in appearance. The artistic aspect was also suffering due to the appearance of leaks, discoloration and the crystallization of impurities on the bronze surface. Accumulations of secondary genesis minerals and oxidations were also identified. But the most serious depigmentation and corrosion of this outdoor monument occurred as the result of pollutant agents: exhaust gas, settled dust, calcified dust and deposition of aerosol particles, characteristic to urban atmosphere.

The present research focuses on the investigation of the composition and morphology of corrosion products layer formed on some bronze screws, originating from the Mathias Rex statuary group, after long-term atmospheric exposure (∼100 years).

2. Experimental

The ten bronze screws investigated in this study were used to assemble the Mathias statuary group and were collected during restoration of the monument in 2010 and analyzed immediately after. They were used to fix the feet of the four bronze characters positioned on the pedestal platform. The spot where the screws were originally placed on the statue group is shown on Fig. 2a. The bronze screws are covered with natural patina formed during 100 years in urban atmosphere of Cluj-Napoca, Romania. Because their advanced stage of degradation (Fig. 2b–c) they could not be reused in statue restoration. Based on optical microscopy observations, it could be noticed that the screws degradation occurred with destruction of the original surface, also with the grain boundary corrosion appearance, which finally leads to alloy embrittlement

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(a) (b)

Fig. 1. Mathias Rex statuary group, Cluj-Napoca, Romania: a: before restoration; b: after restoration.

[1]. Between the measurements, the screws were preserved from moisture and contamination by keeping them in a box containing silicagel, at 22 °C.

The screw surface is colored in gray, brown, and dark green, in concordance with the characteristic bronze patina color [1].

The chemical composition of bronze screws used for experiments was determined by X-ray fluorescence analysis (XRF). Analyses were performed using an installation type InnovX System Alpha Series with W anticathode, at 30 kV, 40 μA, exposure time 60 seconds. SEM analysis were performed with a Scanning Jeol JEM5510LV (Japan) coupled with Oxford Instruments EDX Analysis System Inca 300 (UK) at 15 kV and spot size 39 μm.

3. Results and discussion

3.1. Chemical composition of bronze screws

The chemical composition of bronze screws used for experiments was determined by XRF. The results show that the alloy of screws is a binary Cu6Sn bronze of the following composition: 91.89% copper, 5.15% tin, 1.25% zinc, 1.04% lead and 0.57% iron.

3.2. Morphological characterization of the natural patina

In order to determine the morphology and the chemical composition of the patina layer formed on the surface of the bronze screw exposed 100 years in urban atmosphere of Cluj-Napoca, Romania, SEM - EDX analysis was performed at different points of the screw's surface and some results are presented on Fig. 3 and Table 1.

A visual inspection of the patina revealed the existence of different greenish coloration of the corrosion products varying from yellowish green to bluish green. According to Robbiola et al. [2], the formation of the natural patina on bronze involves three steps: a fast dissolution step, a second one, controlled by the migration of the ionic species and a third one, corresponding to ageing of the previously formed compounds.

Analyzing the SEM images from Fig. 3 taken at different magnifications it can be observed a relatively uniform distribution of the corrosion products all over the surface and the existence of cracks in the patina layers, proving its discontinuity. The corrosion product layer formed is porous with tendency to retain particles of different contaminating products (dust, airborne particles). Atmospheric particles usually incorporated in bronze patina originate from building walls; also alumina, iron oxide, silica and soot are often reported [3].

EDX spectra recorded at different points of the surface allowed to conclude about the composition of the patina layer present on the surface of the bronze screws. As can be seen from Table 1, the distribution of the chemical elements differs from one area to another, as a function of the intensity of the corrosive attack.

The EDX analysis at different points indicated the presence of copper, oxygen, carbon and silicon, whereas Al, S, Fe, Ca, K, P, Mg were present as minor elements. It can be noticed a high percentage of oxygen in the analyzed corrosion products layer, presuming the formation of other corrosion products apart from cuprite, Cu_2O (possibly brochantite [4]) on the bronze surface.

The SEM images (Fig. 3) of bronze screw exhibited two different areas: a dark one (spectrum 4) and light area (spectrum 5). The dark area contained mainly carbon, oxygen and copper. This fact suggests the formation, in the patina layer, of copper carbonate [5]. Also, contrarily to light areas, this area contains 1.89% zinc. Whereas light area is richer in silicon (10.73%) than dark area (which is 3.23%), it also contained more carbon and less copper. Thus, it was concluded that the corrosion layer is not chemically homogenous.

(a) (b) (c)

Fig. 2. Bronze screw from Matthias Rex statuary group: a: the original place of the screw; b: the bronze screw; c: details of the screw.