

TIME ANALYSIS OF KING MATTHIAS THE 1ST SCULPTURAL GROUP

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Abstract

The paper presents a study on the degradation of the King Matthias I sculptural group, caused by environment factors and influenced by the casting technology and by the assembling method. During this study, samples from inside the statue were used and analyzed, using microscopy and X ray diffraction.

Keywords: bronze casting, corrosion, microscopic analysis, copper alloy, bronze time patina

Introduction

The King Matthias the 1st sculptural group is one of the most representative sculptures in Cluj Napoca, Romania. It consists of an equestrian representation of the king, on a stone pedestal and in front of him, with an attitude of worship, holding flags are Blasiu Magyar, an old army leader, Paul Chinezu, Ștefan Zapolya and the ruler of Transilvania, Stefan Bathory. The whole statuary group presents remarkable plastic properties and the equestrian figure impresses by its monumental stillness [1].

The monument is the creation of Fadrusz Janos, a Slovakian artist, who was the disciple of Edmund Heller. He became famous soon after his first work, a cross exhibited in the in Art Museum in Budapest in 1891. His most famous work is the King Matthias the 1st sculptural group, which received first prize in the 1900 World Exhibition in Paris (Fig.1). The group of statues was unveiled, in Cluj Napoca, in 1902.

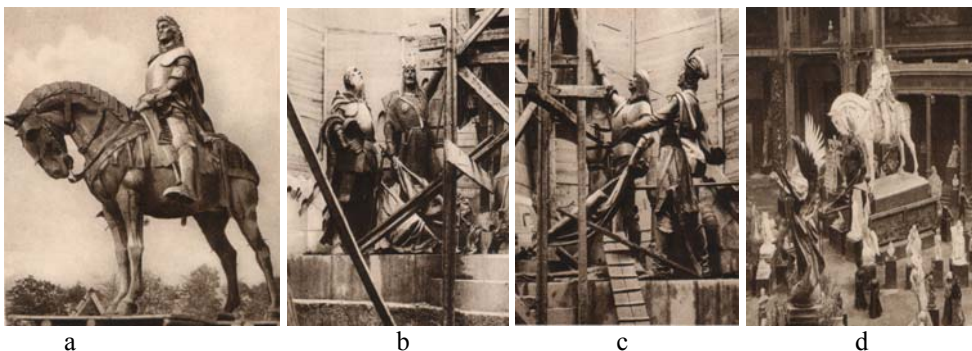


Fig. 1 King Matthias the 1st sculptural group: a), b), c) Images representing the mounting of the statuary group, d) The 1900 World Exhibition in Paris

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The statues were made of bronze on a metal frame and according to the laboratory analysis, the composition of the alloy varies in different parts of the statue. There are variations in the percentage of tin, zinc, lead, but the content of copper exceeds 90 % of the alloy in most cases (Table 1) [2].

Table 1 The chemical composition of the alloy used in the casting of the King Matthias the 1st sculptural group

	Sn %	Pb %	Zn %	Cu %
Sample 1	7,17	0,08	0,36	rest
Sample 2	8,00	0,52	1,30	rest
Sample 3	7,72	0,41	0,21	rest

The statue is 12 m high and 16 tones of alloy were used to create it. The thickness of the shell varies between 8 and 15 mm. The sculptural group is under restoration. In order to establish the status of degradation, the abdomen of the horse was opened to facilitate access to the fittings. Gaining access inside the statue allowed us to study the technology used during the casting process. Moreover, several samples were taken to examine the degradation of the copper used by the old masters.

Each component of the group is made of several pieces assembled together with steel screws (Fig.2). The molding was made using the classic casting technology in sand and for more complex details the wax method was used.



Fig. 2. Images depicting the inside of the sculpture

Degradation factors

The degradation of the bronze used in great works of art is a complex phenomenon which involves various electrochemical reactions triggered by several factors such as: environment

pollutants, the composition of the alloy, the micro-structure of the metallic material, humidity, the degree of surface processing, temperature and surface exposure time [3-5].

Studies have shown that the corrosion agents on a copper alloy surface are oxides, sulfides, carbonates, chlorides, sulfates of copper. Degradation caused by atmospheric corrosion depends on the chemical composition of the metallic material, on the pollutants and on the exposure time needed for the development of corrosion products [4-7]. Degradation appears mainly because of the interaction between water and corrosive substances on the surface of the materials. In the case of King Matthias the 1st sculptural group, the degradation occurred not only because of environmental exposure, but also because of the steel screws used to assemble the component parts, which caused galvanic corrosion (Fig.3).



Fig. 3. Images representing the inside of the sculpture

Materials and Methods

For metallographic analysis the samples were polished with alumina paste and washed with ammonia cupric chloride and with nitric acid, to determine their structure. Our research involved optical microscopy (OLIMPUS GS 51) and X-ray diffraction (DRON-3 diffractometer).

Results and discussions

The structure of the alloy used is homogeneous, the crystals have polyhedral appearance with macles (Fig 4), leading to high anti-corrosive properties [8]. We can observe that in figure 4b, the oxide layer is 10-50 µm thick.

X ray diffraction examination (working conditions): DRON-3 diffraction device, Bragg - Brentano installation, acceleration voltage 25 kV, 20 mA electric intensity, detector voltage 600 V, slits 8,6,0.5,6 mm, wavelength $\lambda = 1.79026 \text{ \AA}$, Cobalt tube.

The main compounds identified after the X ray diffraction analysis in the bronze used to cast the King Matthias I sculptural group are cuprite and tenorite. These are the most common

corrosion products and they are usually found on metal surfaces. Alongside copper oxides, copper was identified in small quantities, probably as a result of cuprite decomposition.

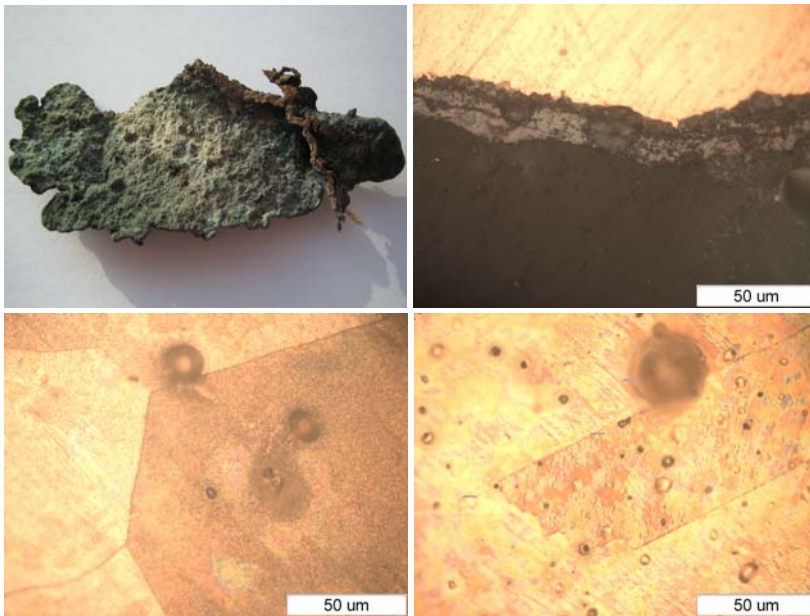


Fig. 4 Samples of the alloy used in the casting of King Matthias I sculptural group: a) raw sample; b) oxide layer; c) macroscopic structure; d) microscopic structure

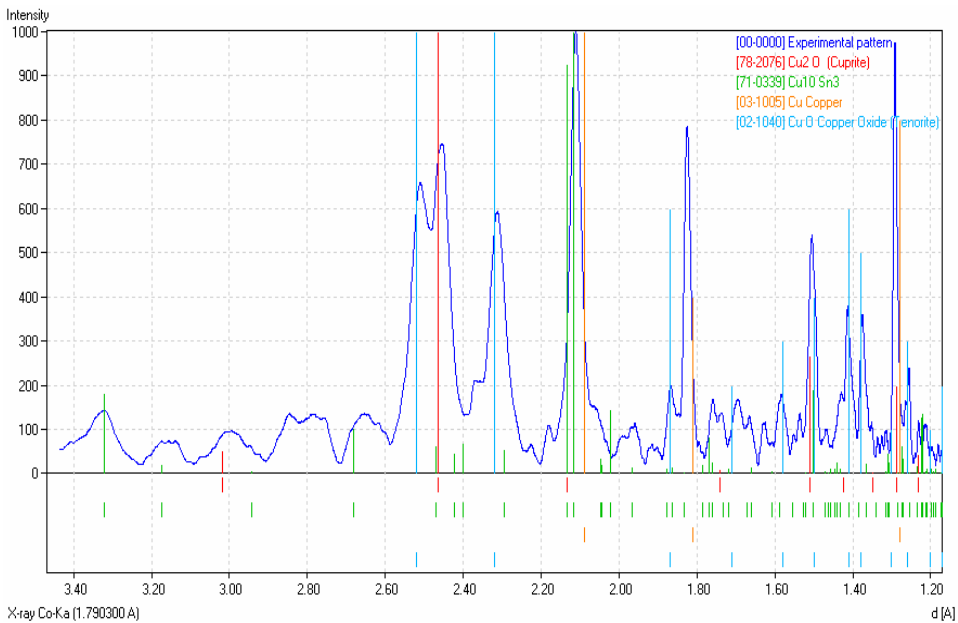


Fig. 5. X ray diffraction analysis of the oxide layer formed on the inner walls of the statue

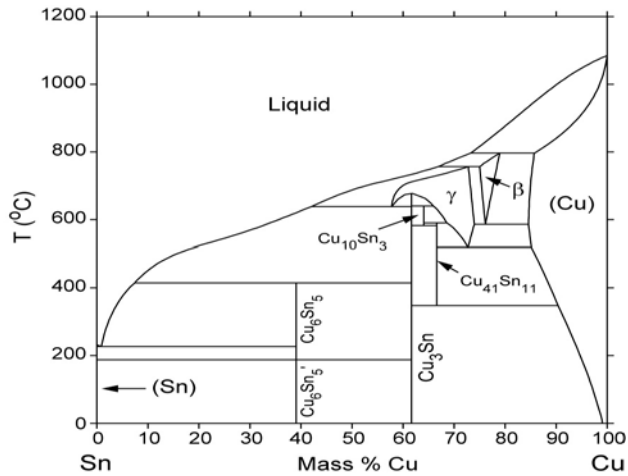


Fig. 6 Phase Diagram Cu-Sn [8]

Table 2. Calculated invariant equilibrium [9-11]

Reaction	Phase	% Cu	% Sn
$\gamma + \text{Cu}_3\text{Sn} \rightarrow$	γ	72.68	27.32
$\text{Cu}_{10}\text{Sn}_3$	Cu_3Sn	61.63	38.37
640.1 °C	$\text{Cu}_{10}\text{Sn}_3$	64.06	35.94

The samples also contain different phases in percentage values: salts, oxides of Mg, Fe, Al which could not be determined.

On the inner walls of the statue large quantities of material sediments were found. After X ray diffraction analysis the sediment was identified as a residual mixture of compounds resulting from contamination: gypsum or calcium sulfate hydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), sulphate calcium (CaSO_4) and quartz (SiO_2). Silicates may have resulted from the molding mixture or from the accumulation of airborne particles. Hydrated calcium sulfate probably resulted from calcium carbonate reaction with sulfate ions.

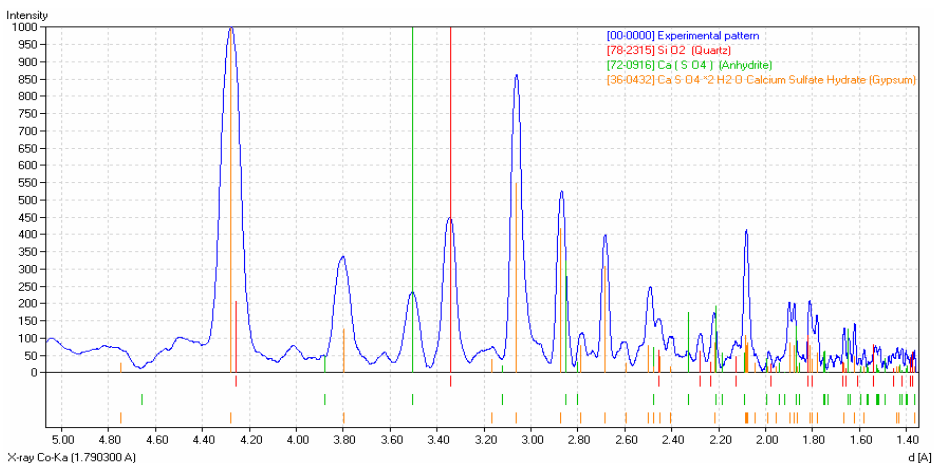


Fig. 7. X ray diffraction analysis of the sediments deposited on the inner walls of the statue

Conclusions

The research has shown that the degradation in the King Matthias the 1st sculptural group mainly occurred because of the casting technique used (on a metal frame) and because of the assembly method (steel screws). The degradation caused by the corrosive agents in the atmosphere was limited, even though the sculptural group was exposed to environment factors for more than 100 years.

The research helped us understand the degradation mechanism of sculptures exposed to atmospheric elements and enabled us to determine a suitable conservation-restoration method for each monument.

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