

THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI. FASCICLE IX. METALLURGY AND MATERIALS SCIENCE N^0 . 1 – 2010, ISSN 1453 – 083X

TIME ANALYSIS OF KING MATTHIAS THE IST 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 through microscopy and X ray diffraction.

KEYWORDS: bronze casting, corrosion, microscopic analysis, cooper alloy, time bronze patina

1. Introduction

King Matthias the Ist sculptural group is one of the most representative sculptures in Cluj Napoca, Romania.

It consists of an equestrian representation of the king lying on a stone pedestal in front of which are represented in an attitude of worship holding flags Blasiu Magyar, an old army leader, Paul Chinezu, Ştefan Zapolya and the ruler of Transilvania, Stefan Bathory.

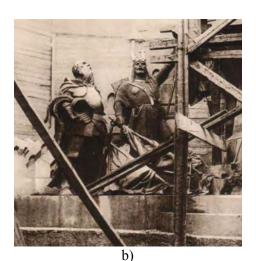
The whole statuary group presents remarkable plastic properties and the equestrian figure impresses through its monumental stillness [1].

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 Art Museum in Budapest in 1891. His most renowned work is King Matthias the Ist sculptural group, which received the first prize in the 1900 World Exhibition in Paris (Fig.1).

The statue was unveiled, in Cluj Napoca, in 1902.

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].





a)



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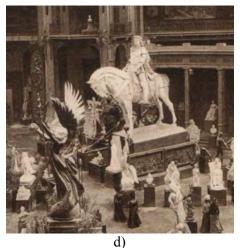


Fig. 1. King Matthias the Ist sculptural group: a), b), c) Images representing the mounting of the statuary group, d) The 1900 World Exhibition in Paris.

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

Chemical	Sn	Pb	Zn	Cu
composition	[%]			
Sample 1	7.17	0.08	0.36	remaining
Sample 2	8.00	0.52	1.30	remaining
Sample 3	7.72	0.41	0.21	remaining

The statue is 12 m high and 16 tones of alloy were used to create it. The thickness of the walls varies between 8 and 15 mm. The sculptural group is under restoration and to establish the status of degradation the abdomen of the horse was opened to facilitate access to the fittings.









Fig. 2. Images depicting the inside of the sculpture.



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The opportunity to enter inside the statue has allowed the study of the technology used during the casting process. Also, several samples were taken to examine the degradation of the copper used by old masters

Each component part 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 lost wax method was used.

2. Degradation factors

The degradation of the bronze used in great art works 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].

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].

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 Ist sculptural group, the degradation occurred not only because of environmental exposure, but also because of the steel screws used for assembling the component parts, which caused galvanic corrosion (Fig. 3).





Fig. 3. Images representing the inside of the scupture.

3. Materials. Working method

For the metallographic analysis, the samples were polished with alumina paste and washed with ammonia cupric chloride and with nitric acid to determine their structure. The structure of the alloy used is homogenous, the crystals have polyhedral appearance with macles (Fig. 4), leading to high anticorrosive properties [5].



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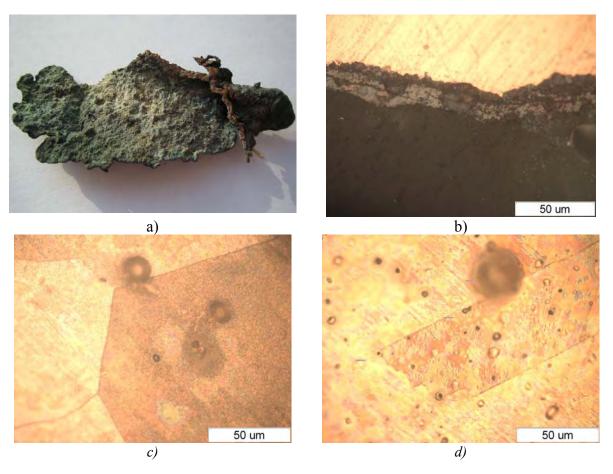


Fig. 4. Samples of the alloy used in the casting of King Matthias I sculptural group: a) raw sample; b) oxide layer; c) macroscopic structure; d) microscopic structure.

We can observe that in Figure 4b, the oxide layer is 10-50 µm thick. Research includes optical microscopy (OLIMPUS GS 51) and X ray diffraction (DRON-3 difractometer). X ray diffraction examination (working conditions): DRON-3

diffraction device, Bragg - Brentano installation, acceleration voltage 25 kV, 20 mA electric intesity, detector voltage 600 V, slits 8,6,0.5,6 mm, wavelenght λ = 1.79026 Å, Cobalt tube.

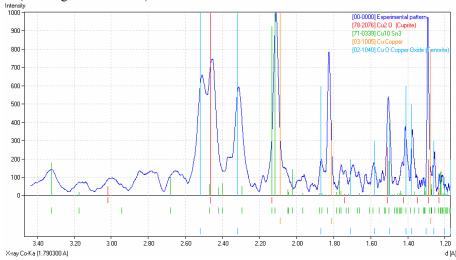


Fig. 5. X ray diffraction analysis of the oxide layer formed on the inner walls of the statue.



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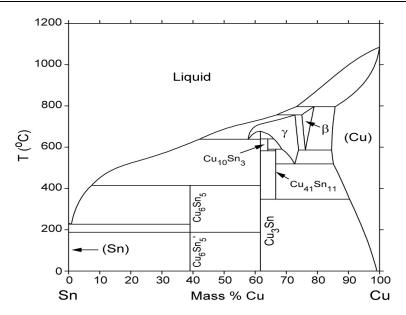


Fig. 6. Phase Diagram Cu-Sn [5].

Table 2. Calculated invariant equilibrium [6]

Reaction	Phase	Cu, %	Sn, %
γ + Cu3Sn -> Cu10Sn3 640.1 °C	γ	72.68	27.32
	Cu3Sn	61.63	38.37
	Cu10Sn3	64.06	35.94

The main compounds identified after the X ray diffraction analysis in the bronze used for casting King Matthias I sculptural group are cuprit and

tenorit. These are the most common corrosion products and are usually found on metal surfaces.

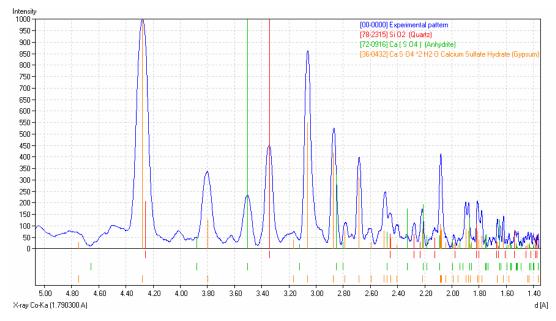


Fig. 7. X ray diffraction analysis of the sediments deposited on the inner walls of the statue.



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Alongside copper oxides, copper was identified in small quantities, probably as a result of cuprit decomposition.

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 the X ray diffraction analysis, the sediment was identified as a residual mixture of compounds resulting from contamination: gypsum or calcium sulfate hydrate $(CaSO_4\ 2H_2O)$, 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.

4. Conclusions

The research has shown that degradation in the King Matthias the Ist sculptural group mainly occurred because of the casting technique used (on a metal frame) and of the assembly method (steel screws).

To a limited extent, degradation is caused by corrosive agents in the atmosphere, even though the sculptural group has been exposed to environment factors for more than 100 years.

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

Acknowledgments

The "PRODOC" POSDRU/6/1.5/S/5, ID 7676 project is thanked for financial support of this work.

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