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Preliminary Alloys Characterization and Technological Interpretation of the Manufacturing Process of the Vittoria Alata di Brescia by means of Neutron Diffraction

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***Abstract* – The Winged Victory of Brescia (Vittoria Alata) is one of the most important Roman bronzes rediscovered in Italy, dated around the 1st Century AD. Since the 19th century, the statue has undergone multiple conservation interventions [1-2]. The latest one started in 2018, owing to an agreement among Comune di Brescia, Fondazione Brescia Musei, Opificio delle Pietre Dure (OPD) di Firenze, Soprintendenza Archeologia Belle Arti e Paesaggio per le province di Bergamo e Brescia. The project was coordinated by the Opificio delle Pietre Dure and offered a unique opportunity for a thorough study of the statue. The composition of the alloy was investigated with a combination of traditional techniques (SEM - EDX; XRF) and neutron diffraction in time of flight. This approach allowed us to clearly characterize the alloy used for the different parts (portions of the body, arms, wings), and to obtain clues on manufacturing methods of the statue.**

I. INTRODUCTION

A. The statue

The Vittoria Alata di Brescia was found in 1826, together with a heap of bronze artefacts (including portraits, pectorals for monumental statues of horses and several frames), in an underground hideout on the western side of the Capitolium of Brescia.

The statue - about 1.94 m high without the pedestal - represents a winged female figure with arms protruded forward writing the name of the winner on a shield (missing) (*Fig.1*). It is a hollow casting bronze, physically separated into five pieces: the body, the two arms and the two wings. Even the wings seem to be obtained by joining two parts cast independently and assembled mechanically. Each wing is in fact composed of a metal plate which constitutes, from an anatomical point of view, the set of primary and secondary flight feathers. This part fits inside a sheath structure that represents the wing wrist and his plumage [3].

The aim of this study is to characterize the alloys that make up the various parts, in order to better understand the constructional techniques of this masterpiece. Furthermore, we will try to locate, if any, additions and repairs and to determine their composition.

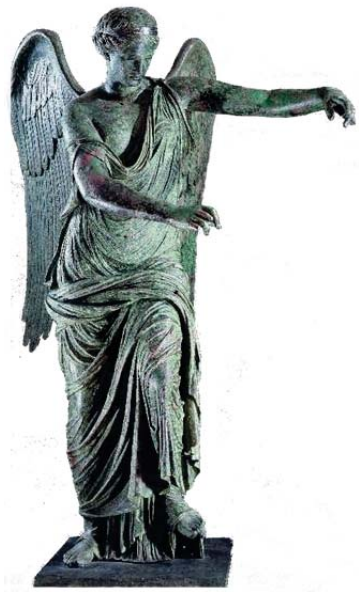

Fig. 1. The Winged Victory of Brescia before the ongoing restoration.

B. Accuracy issues in quantitative evaluation of an archaeological copper alloy by means of traditional analysis.

Studying the alloy composition of an archaeological bronze is a complex problem, due to the manufacturing in pieces not always identified, cast inhomogeneity, and uneven depth of corrosion penetration [4]. In an effort to overcome these problems, twenty micrometric samples of metal were taken from different areas of the artefact, aiming at achieving the maximum of representativeness while keeping invasiveness at minimum. All the samples described in this paper were analysed at the Scientific Laboratory of OPD by means of Scanning Electron Microscope-Energy Dispersive X-Ray probe (SEM-EDX). Observations of samples in cross-section with the SEM show the limitations of an approach based exclusively on the amount of X-radiation emitted by the individual atomic species for the alloy characterization of an archaeological bronze.

For example, in Figure 2, the dark field optical microscopy image of the M1 sample is shown. The layered structure from left to right shows: calcium and copper silicates, copper carbonates and hydroxycarbonates, copper chlorides, lead carbonates and hydroxycarbonates in the outer layer, a strip of cuprite (reddish violet in the figure), and an area enriched in tin (which appears orange due to the contribution of Pb and Sn oxides and cuprite). The latter corresponds to a layer where the alloy has lost part of its copper content, which has been transformed into mineral phases (decuprification layer) [5].

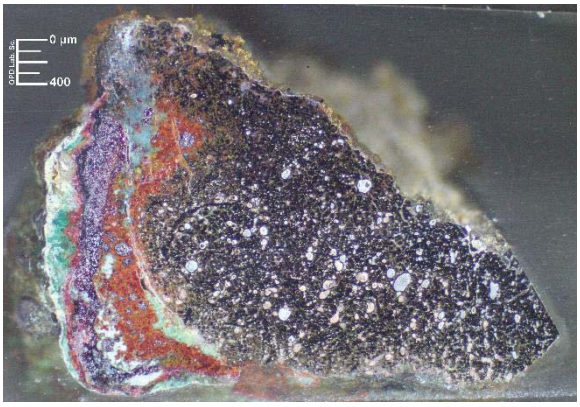

Fig. 2. Dark field optical microscopy image of sample M1. As can be seen in the figure, the alloy fragment is deeply affected by mineralization phenomena that propagate from the surface to the bulk.

Although in sample M1 the mineralized areas appear well localized, the decuprification phenomenon could have a very irregular shape extending to the interior of the artefact along the grain boundaries.

The variable depth of the internal corrosion may make it difficult to quantify accurately the alloy with elemental techniques and possibly lead to an overestimation of the tin content (*Fig.3*).

As samples of an archaeological bronzes may be largely affected by the problem of variable depth of internal corrosion, it is of remarkable importance to set an analytical protocol that can identify and quantify the crystalline phases of the alloy, regardless of the state of conservation of the metal, and, at the same time, provide a detailed description of morphological features.

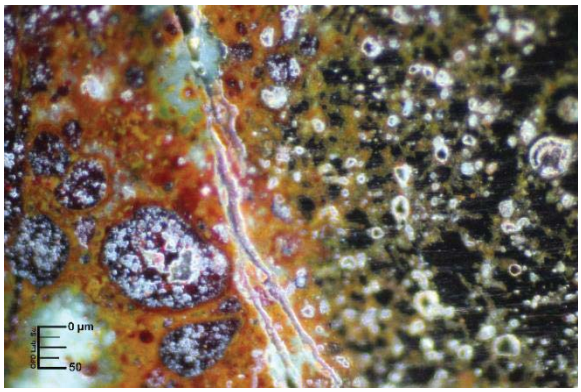

Fig. 3. Dark field optical microscopy image of a detail of the M1 sample. The image shows how decuprification phenomena travel deep into the bulk of the metal, occupying porosities, cracks or interstitial space between the crystallographic grains. The tin-enriched decuprification areas appear orange due to the contribution of Pb and Sn oxides and cuprite.

II. TIME OF FLIGHT-NEUTRON DIFFRACTION

In order to obtain high accuracy quantitative phase analysis, details about dendritic compositional gradients, and casting related microstructural features (columnar growth, crystalline defects density and crystallographic domain size), we performed time of flight neutron diffraction analysis at the INES beamline located at *ISIS neutron and muon source* in the United Kingdom, under the supervision of Dr. Antonella Scherillo [6]. Time of Flight Neutron Diffraction allows to measure selected areas of the samples (without any pre-treatment), in a range from a few mm to a few cm, and to quantitatively determine the concentration of the crystalline phases present in the investigated volume.

Furthermore, by studying the shape and relative intensity of the diffraction peaks in the metal phases, it is possible to obtain, indirectly, information on the grain size, on the presence and density of defects and internal stress, and on the processing or solidification directions [7].
To support the investigations carried out by ToF-ND we have used also the Nuclear Resonance Capture Analysis (NRCA) [8], which provides a semi-quantitative analysis of the elements present in the volume of the sample investigated.
Both techniques are non-invasive and can be performed on selected areas of whole objects but, given the impossibility of moving the statue to the neutron source, we opted for the use of sampling fragments. A piece of the terminal feathers of the left wing, (the only macro component detached from the statue – about 3.0 cm x 3.5 cm) was also analysed.
The data analysis was performed using Mantid code for the preliminary data processing and the analysis of resonant capture data and GSAS through the EXPGUI interface for the analysis of the diffraction data to obtain the multiphase and microstructure quantitative analysis. The alloy composition was determined using the calibration curves published by Grazzi et alii, in 2010 [7].

III. SAMPLES DESCRIPTION

Twenty samples were taken with the intent to represent all parts of the artifact; however, the conservation status and the inaccessibility of certain areas have forced us to renounce the sampling of some parts. Unfortunately, among these, no fragments could be obtained from the head. The sampling was set in total respect of the work of art, choosing areas that are not visible. Almost all the samples were taken from inside the statue, except for the M1 and M2 samples, removed respectively from the inner edge of the left foot, and from the fractured edge on the left side.

During the sampling operations, it was possible to observe that even the inside of the bronze surface is extremely mineralized; in some areas, it was necessary to engrave even 2-3 mm before finding the sound metal. The sampling points are shown in the illustration in Figure 4.

All samples are between hundreds of microns and a few millimetres in size, and weigh between 0.09 g and 3.5 g.

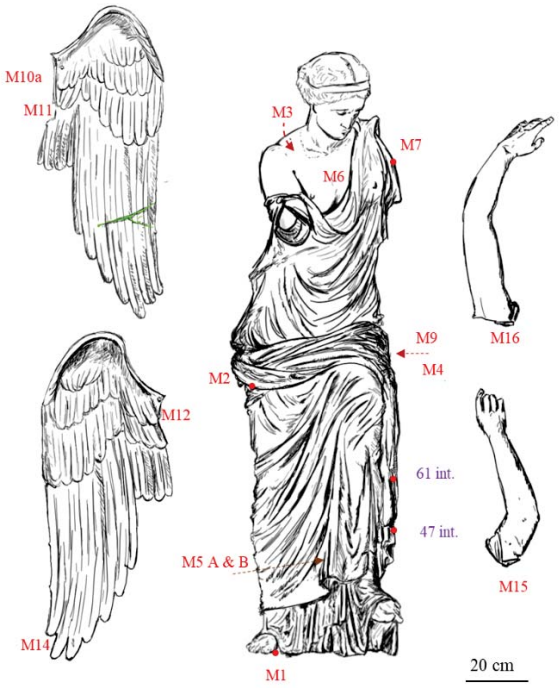

Fig. 4. Illustration of the statue sampling points

A feather fragment of the right wing has also been analysed (*Fig. 5*).

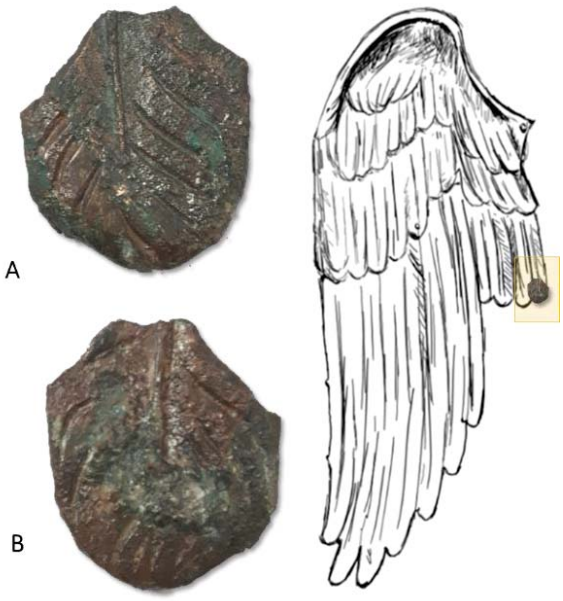

*Fig. 5. Feather fragment of the right wing of the Winged Victory: **A** front, **B** back. On the right in the figure the point of detachment of the fragment from the rest of the wing.*

IV. MAESUREMENT CONDITIONS

The samples were wrapped in aluminum sheets (transparent to neutrons) and mounted on a motorized frame that allowed the consecutive measurement of various samples. Depending on the volume and mass of the samples, different measurement times were selected which ranged from 1 to 30 hours of irradiation. The feather fragment was analysed in two different areas: next to the tip of the feather, and in the middle of the fragment on the rachis of the feather (*Fig.* 6).

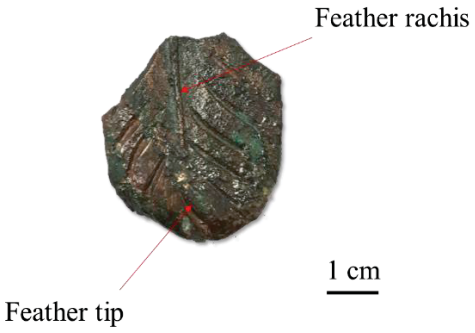

Fig. 6. Measurement areas of the feather fragment of the right wing.

V. PRELIMINARY RESULTS

Neutron resonance capture analysis (NRCA) made it possible to determine the elements present in the alloy. Due to the too small sample size, the statistics of some data are too low to identify resonance peaks of the elements.
The results obtained are shown in the table below (*table 1*).
The absence of certain elements in some samples does not automatically imply their absence in the alloy, but indicates only that low statistics was achieved for them. The main elements identified are copper and tin: silver, antimony and arsenic appear as minor elements or as traces.

Table 1. NRCA results.

Sample	**Elements**				
Feather tip	Cu	Sn	Ag	Sb	As
Feather rachis	Cu	Sn	Ag	Sb	As
1 M	Cu	Sn			
2 M	Cu				
3 M	Cu				
4 M	Cu	Sn	Ag	Sb	As
5 M	Cu				
5 M a	Cu	Sn	Ag	Sb	As
6 M a	Cu				
7 M	Cu	Sn			
8 M	Cu				
9 M	Cu	Sn			
10 M a	Cu	Sn	As		
10 M b	Cu	Sn			
11 M b	Cu	Sn	Ag		
12 M					
12 M a					
14 M					
15 M	Cu				
16 M	Cu	Sn			
47 int	Cu				
61 int	Cu	Sn			

After screening the samples with NRCA, the acquisition and processing of the ToF-ND data showed the presence of the following phases:

- Alpha phase of the bronze with FCC structure. When there are dendrites with significant statistics, a two-phase fit was made to take into account the two different diffraction figures generated by the low and high tin content components
- Lead phase with FCC structure.
- Cuprite phase (copper oxide).
- Nantochite phase (copper chloride).
- Chalcocite phase (copper sulphide).

Notwithstanding the presence of internal corrosion and the small size of the samples, the technique allowed to identify the composition of the bronze and to start a discussion on the possible origin of differences among the samples.
The concentration of lead in all the samples was also determined and compared with SEM-EDX results: the samples show a variable content that ranges between ~ 4% wt and 12% wt for ToF-ND and between ~ 5% wt and 10% wt, for SEM-EDX analysis.

This extreme variability was observed, not only between different areas of the statue but also on a very short scale.

Furthermore, as in the case of sample M1, changing the stratigraphic plane (thus lowering the section plane by a few tens of μm), lead concentration detected by SEM – EDX changes from ~ 2% wt to 6.1% ± 0.1 wt. The causes of this uneven distribution can be several. They can originate either from the casting process or from the burial. The latter favours the formation of carbonates and hydroxy carbonates of Pb, which can be found a few hundred microns below the surface concretions, affecting the sound metal itself.
Lead will therefore not be considered a reliable element for characterizing and comparing different alloys on this artefact, and tin concentration only will be used instead.

VI. AKNOWLEDGEMENTS

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