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CONSERVATION OF COPPER ALLOYS ARTEFACTS FROM ARCHAEOLOGICAL EXCAVATION

Maura Mereu*, Vilma Basilissi*, Giuseppe Guida*,
Massimo Vidale*, Maria Pia Casaletto**,
Gabriel Maria Ingo**, Luciana Drago***, Enrico Greco ****

* Istituto Superiore per la Conservazione ed il Restauro, Rome (mauramereu@gmail.com)

** CNR-ISMN, Istituto per lo Studio dei Materiali Nanostrutturati

*** Sapienza, University of Rome

**** University of Catania, Department of Chemistry

Abstract

The conservation work on the pilgrim's flask from Casale del Fosso necropolis is a part of more comprehensive study project, which aims to examine issues that are connected to archaeological metals and its conservation problems. From the conservative point of view the main interest is directed toward the testing of new molecules, already developed by the National Research Council, in the stabilization phase of archaeological artefacts. In order To perform this study a group of objects in copper alloy, including the flask, from the necropolis of Veio-Casale del Fosso have been already selected and analyzed

Keywords: Copper alloys, Corrosion, Inhibitors, EDXRF, XRD

INTRODUCTION

All archaeological artefacts as a vehicle of information are a *moyen d'accès privilégié à la conoissance du passé*[1]. In particular, the metallic objects exert a dual role; an intrinsic historical value and also an evidence of the advanced skills required for their construction. Every conservation work is aimed at the acquisition of such information that will be used as a means to provide the long-term preservation of finds and at the same time, their readability and presentation.

It is not always easy to achieve these objectives. Since at the time of discovery the metal finds are usually heavily modified due to corrosion: volume, shape, weight and mechanical properties change during the period of burial, most often are illegible, the contact with the new environment causes the change of the previous balance and thus the reactivation of corrosion.

1 Berducou 1990, p. 15.

At this point there are two main problems: cleaning (exactly the right level of cleaning which stop) and the stabilization of the find material about the corrosive processes in progress.
Regarding cleaning, the right level coincides to the identification of the original area, a concept that has been the focus of several studies. in this context is associated to a physical structure that can reveal information such as decorations and qualifications of surface processing signs, signs of use, etc.., and therefore must be preserved and studied. The difficulty of this identification is mainly due to non-uniformity of corrosion processes and the morphology of corrosion products, which can cause lags or even "mixed up" levels which constitute the original area. All of these problems contribute to make complex the determination of the layers of corrosion products. Because exists a limit beyond which you cannot find the original surface, its exact identification is conducted with reference to various parameters that are related to: formation of corrosion products (some are often located near of the original surface), presence of decorations or surface treatments, contact between different parts of the object or objects nearby. In the cases where recognition of these indices was difficult, then the location of the area will be established as a hypothesis.
The stabilization of the material, ie those treatments finalized to slow down the natural process of corrosion is one of the most difficult phases of conservation. Very often the archaeological copper alloys have a pronounced electrochemical corrosion caused mainly by the presence of unstable species (active chlorine). In general, these species are located in depth, at the interface between the core metal and corrosion products. In environmental conditions of high humidity these species reactivated the mechanism of degradation. The state of conservation of artifacts is so irremediably compromised.
The corrosion is manifest in attacks very focused and deep (so-called pitting), whose main characteristic is just to develop under the corrosion products, penetrating deeply into the alloy, with typical pinpoint forms (pit) or-and craters appear on the surface. The treatment options are varied and can work directly on the pitting phenomenon or extract, as much as possible, chlorides and then apply a treatment of inhibit corrosion. For this purpose the corrosion inhibitors are used, a group of substances that are theoretically able to stabilizing the active corrosion process. Some problems were identified for their use as the impossibility of application on all types of findings or the inconstancy of their efficacy and especially the risks to health.
However, in this period there is a wide field of studies in continuous evolution based on the problem of the stabilization. In most cases, research are still confined to an experimental context. Industrial compounds are tested first on standard samples and only after on original finds, with a proposed action protocol. These experimentations have the objective of evaluate the effects, interactions and mode of application of the new compounds that could be corrosion inhibitors. This is the way followed by the laboratories of the Institute for the Study of Nanostructured Materials of CNR, engaged in the development of new molecules, that promising good results.

EXPERIMENTAL

The study was performed at the Superior Institute for the Preservation and Restoration (Rome) which provided an opportunity to start a project of cooperation between the different institutions this study tried to get the archaeometrical data pertinent to the archaeological copper alloy selected for the pilot phase. It is a homogeneous group of artifacts, including the pilgrim's flask, dating from the end of the 8th century BC, from the exceptional burial area of Casale del Fosso (Veio). The conservation interest of these important documents of the material culture is joined to a study of technology and exchange that occurs the metallurgical production.

Every conservative approach needs appropriate planning, which includes the choice of most appropriate interventions as a next step to the documentation and diagnostic tests. The intervention, defined in relation to product with the objective of provide its long-term conservation, the readability, the presentation, and allow the acquisition of information of the object. This implies a large knowledge of the object through the macro and micro structural characterization.

The macrostructural characterization starts with a detailed examination of the object through an accurate visual observation. The aim is to identify the manufacture, its function ,its use through the identification of its technological characteristics (size, shape, traces to decoration, presence to organic material, traces to work and use, old restorations, completeness of its archaeological profile) and its conservation status (study of the constituent materials, analysis of degradation phenomena and the characteristics of corrosion products). The observation must always accompanied from the record to every detail considered important, through a detailed photographic and graphics documentation. In this first analytical step is important the realization of cleaning tests to identify, through the stratigraphy of the corrosion products, the original surface and determine the most appropriate cleaning method.

The micro structural characterization provides important information about the materials of metal archaeological artifacts.

It involves the use of qualitative and quantitative analysis and comparison of data with those obtained for similar types of artifacts and historical context. In the Italian context, the archaeo-metallurgic sector is a recent field of research that had attracted interest and limited production to specific cultural and historical contexts, one of these is the case of as copper alloy finds mainly worked to hammer of the early Iron Age that are off of interest of this research. Important here is the work of Cristiano Iaia who collected all "*the available data on the composition of metal hammer made objects (...) from central Italy (Etruria, Lazio,Marche)*" from "*both contexts of the first Iron Age that early in the second Iron Age, or Orientalising*" adding that "*the large chronological gap in the sources and the differences of methods of analysis used in these cases certainly influencing the comparability of data and decrease its the value.*" From his studies emerged as the laminated parts are made of "*a sufficiently ductile and malleable alloy that should not lead to breakage either during the hammer working, or*

in use"[2], in which the average percentage of tin is 8,6%, a level relatively high and even higher for the finds from Veio, which however supplied to the league the best characteristics to be submitted to mechanical stress.
On all selected finds has been carried out the energy dispersive X-ray fluorescence (EDXRF) on three of the six samples have been observed with metallographic microscope while the other three were submitted to X-ray diffraction. All investigations has been conducted at the Laboratory of Chemistry of Superior Institute for the Conservation and Restoration in Rome. The finds were initially chosen according to the supposed technique of production and were divided in two groups, one consisting of artifacts obtained by melting, the other group composed of artifacts obtained by alternating cycles of mechanical and thermal processing. The first group consists of three fibulae (T1000) and one ring (T857), the second group, largest, consist of two spiral bracelets (T1000), one piece of coating lamina, part of a wagon (T872), six big studs (T872), (one, the n. 3, was submitted to metallography). Finally, the pilgrim flask from the grave 962.

RESULTS

The Energy Dispersive X-ray Fluorescence (EDXRF) has been performed on 15 objects described above. The faleres have been analyzed in two different sites, since it has hypothesised a different composition between the lamina and the nail in the middle. The Table 1 reports the results of XRF with qualitative and semi-quantitative characterization indicated in percentage by weight. We know how the technological advancement of Etruscan bronze alloy is evident by well-defined composition and depending of the processing technique. Generally we can found for the laminates a content of Sn around 8%, while for the melted objects 8-12%. The data shown in the Table 1, for all of the samples, are not compatible with these standards, certainly distorted by depth of corrosion. Therefore, in order to understand the correct data, the quantitative analysis needs to consider the size and the extension of the corrosion present on these objects. Considering the percentage of copper (Cu) present in the fibulae made by melting, the amount reached in the case of No. 36233 equal to 56.1% is very significant. Instead we can see that the composition of faleres is comparable to the standard percentage of copper between 80,3 % and 88,8%.
The results of EDXRF analysis (Table 2) performed on samples of the pilgrim's flask confirm the presence of a binary copper-tin alloy accompanied by anomalous values of zinc, which must be attributed to the restoration materials. A control analysis has been even carried out on the fragment in the back where there are residues of substances attributed to previous restoration. It show very high values of zinc, accompanied by significant percentages of arsenic.

2 Iaia, 2005, p. 24.

Table 1. Studied findings

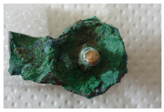
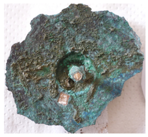
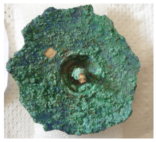
N° Inv.	Findings	Analysis	N° Inv.	Findings	Analysis
36233 (T 857) fibula		XRF	36498 (T 872) stud-nail		XRF
37144 (T 1000) fibula		XRF	36498 (T 872) stud		XRF
37173 (T 1000) fibula		XRF	36497 (T872) stud		XRF metallog- raphy
36230 (T 857) ring		XRF	36496 (T 872) stud-nail		XRF
36232 (T857) stripe		XRF metallog- raphy	36495 (T872) stud-nail		XRF
37150 (T 1000) bracelet		XRF	36494 (T872) stud-nail		XRF
37152 (T1000) bracelet		XRF metallog- raphy	36493 (T 872) stud-nail		XRF
36500 (T 872) fragment		XRF			

Table 2. EDXRF results

Finds	Cu%	Sn%	Pb%	As%	Ag%	Sb%
36233 (T857) – fibula	56.1	34.7	6.2	1.4	0.2	1.3
37144 (T1000) – fibula	89.4	8.8	1.5	0.3	0.0	0.0
37173 (T1000) – fibula	83.1	15.8	0.8	0.3	0.0	0.0
36230 (T857) – ring	79.8	17.8	1.8	0.5	0.0	0.0
36232 (T857) – stripe (P1)	74.1	25.1	0.6	0.2	0.0	0.0
37150 (T1000) – bracelet	69.3	25.6	5.0	0.0	0.1	0.0
37152 (T1000) – bracelet (P2)	78.8	20.7	0.5	0.0	0.1	0.0
36500 (T872) – fragment	86.1	13.2	0.6	0.1	0.0	0.0
36498a (T872) – stud (nail)	85.9	13.6	0.5	0.0	0.1	0.0
36498 (T872) – stud	80.9	16.4	2.6	0.0	0.1	0.0
36497 (T872) – stud (P3)	82.3	17.2	0.4	0.0	0.1	0.0
36496a (T872) – stud (nail)	81.2	17.2	1.5	0.0	0.1	0.0
36496 (T872) – stud	85.9	13.2	0.9	0.0	0.1	0.0
36495a (T872) – stud (nail)	82.9	15.8	1.2	0.0	0.1	0.0
36495 (T872) – stud	88.8	10.5	0.7	0.0	0.0	0.0
36494a (T872) – stud (nail)	80.6	17.7	1.7	0.0	0.0	0.0
36494 (T872) – stud	81.6	17.1	0.9	0.4	0.0	0.0
36493a (T872) – stud (nail)	80.3	18.1	1.6	0.0	0.0	0.0
36493 (T872) – stud	86.8	12.5	0.5	0.2	0.0	0.0

The analysis of the patinas conducted by X-Ray Diffraction (XRD) on a piece of nail (probably a stud) (Fig. 1), on a fragment of fibula (Fig. 2) and on a fragment of the flask (Fig. 3) showed a uniform condition which demonstrate the presence of cuprite [Cu_2O] and malachite [$Cu_2CO_3(OH)_2$]. the homogeneity of the patinas is attributed to the environmental characteristics of the discovery context. The analysis performed on the restoration material (Fig. 4) of the sample No. 19 showed the presence of copper (II) acetoarsenite [$Cu(C_2H_3O_2)_2 \cdot 3Cu(AsO_2)_2$] (an emerald green artificial pigment also known as Paris green, which has a very good covering power and mainly used in the restoration in the '50s) gypsum, illite-montmorillonite, calcite, quartz and zincite.

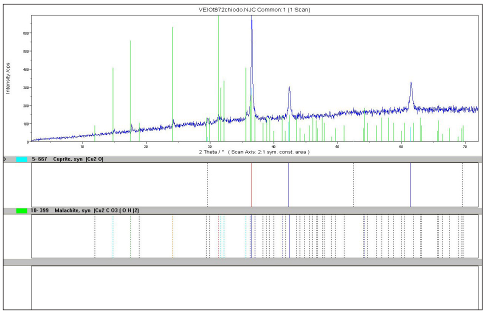


Fig. 1: XRD on a piece of nail

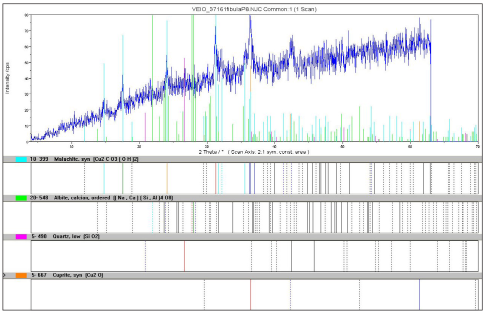


Fig. 2: XRD on a fragment of fibula

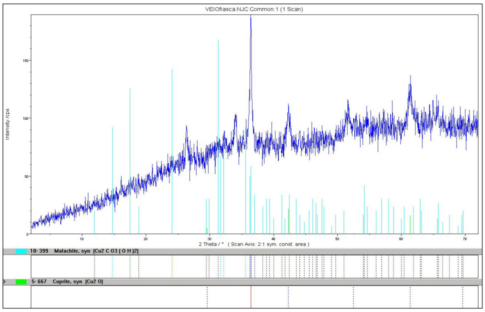


Fig. 3: XRD on a fragment of flask

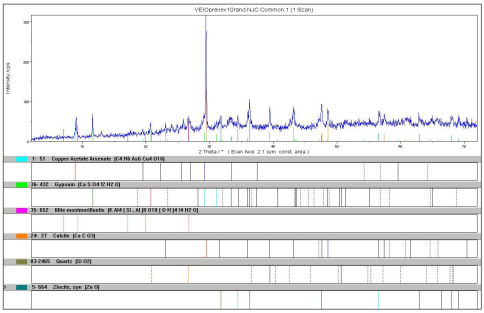


Fig. 4: XRD of restoration material

On the two groups of finds have been performed three samples of the alloy that have to be submitted to metallographic observation. Crystal structures with polygonal grain and traces of geminate are visible (Fig. 5), which testify that occurred a thermal and mechanical processing. In addition to information of technology has been possible to determine the state of conservation of objects, identifying the type and the entity of corrosion. It's possible to observe the thickness of corrosion products and the size of intergranular and intragranular corrosion processes (Fig. 6). We know that the first are particularly insidious and dangerous because of their invisibility on the surface and also because they may compromise the mechanical strength of the object. Furthermore this type of corrosion, especially if accompanied by intragranular corrosion, imposes an adequate intervention to guarantee the preservation of the manufacture.

The studies carried out in this context provides an excellent opportunity to start and explore the conservation problems we discussed above and the systematic analysis of the constituent materials and manufacturing techniques.

The artifacts analyzed in this study are an homogeneous group of copper alloy finds, dating to the second half of the 8th century BC and coming from a single context, the necropolis of Casale del Fosso (Veio). This is a wide and important burial area where have been found graves belonging to people of upper society, involved in the management of trade and the movement of assets (metals, livestock, slaves, wine), who remarked their qualification status through a military outfit and at the same time by exhibition of exotic products like the pilgrim's flask. It represents the most significant findings and at the same time the most compromised by the conservative point of view. For this reason we decided to submit it to a long and complex restoration work still in progress.

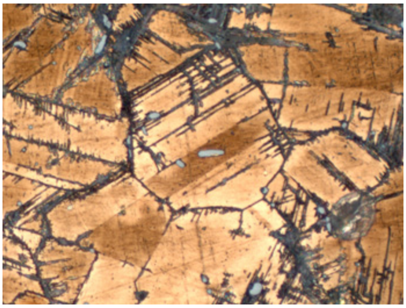


Fig. 5: Crystal structure with polygonal grain, geminate and intergranular corrosion of find No. 37152 (500X).

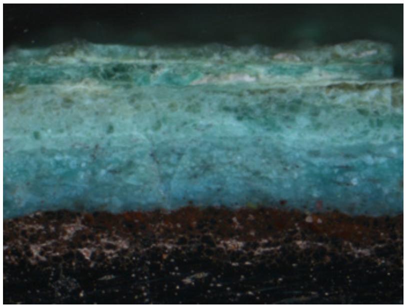


Fig. 6: Phase-contrast image of the thickness of corrosion products of the find No. 36232 (50X).

RESTORATION PROJECT AND CONCLUSIONS

The operation become difficult for two reasons: the conservation status of the constituent materials and the previous restoration, which was damaging for the preservation of the object. The pilgrim flask can be dates from the end of 8th century BC. It was made by assembly of several thin sheets of embossed copper alloys. The thickness of the sheets is 0.5-1.2 mm. The flask has been found in fragments during the excavations of the necropolis of Veio, in 1915-1916. Therefore it has been restored following the mimetic principles. Today we have two parts of the sides of the flask, a large fragment of the back face full of gaps, some fragments of the lateral parts and of the neck. All these parts have been pasted on a circular paperboard that reproduces the original form (Figs. 7-8).
The conservation status of the flask is very critical. The sheet is mineralized and cracked in several places. On its surface there are a lot of dirt and materials from the previous restoration. Furthermore, portions of the base are deformed and this caused the detachment of fragments of the sheet (Figs. 9-10).
The plan for treatment, still in progress, including the removal and restoration of the original fragments of the flask and creating a new base, it is needed for the preservation and exposure of the object.

Fig. 7: Front face.

Fig. 8: Rear face.

Fig. 9: Deformation of the base and loss of some parts of the bronze sheet.

Fig. 10: The detachment of fragments and highlighting of the base.

The surface was completely cleaned using a scalpel under stereo microscope (Fig. 11). In this way has been possible to eliminate extraneous material surface, revealing the original color of the patina, define the limits of integration and find the technical expedients used in the previous restoration. In order to reproduce the embossed point of decoration they used a small concave hemisphere of lead then covered with gypsum and pigments (Fig. 12).

The component parts of bronze small sheet have been temporarily bonded with thin strip of Japanese paper soaked by ethanol and placed on the surface of the sheet. The component parts small sheet of bronze have been temporarily bonded with thin strip of Japanese paper soaked by ethanol and placed on the surface of the sheet (Fig. 13).

In the next step we would create a cast of the back of the flask in order to make the tilting of this side and cleaning easier. at that time it was possible to move from its base. Before doing this, the back surface has been protected by strips of Japanese paper. Two tests have been performed to seal the protected area and make the cast (Fig. 14). In the first test was realized using microcrystalline wax, in the second test we used a very thin layer of wax. Subsequently, silicone rubber has been poured on the flask in order to obtain an accurate cast of the decorations.

All steps have been documented by digital photos and drawings created by AutoCAD software.

Fig. 11: Clearing surface by scalpel.

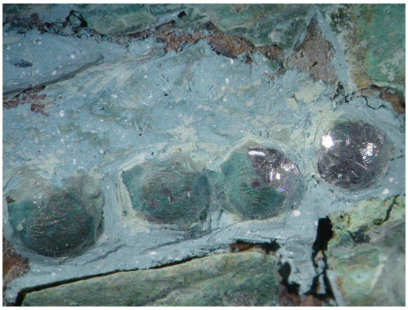


Fig. 12: Technical expedients used in the previous restoration.

Fig. 13: Fixing the broken points using glued and Japanes paper.

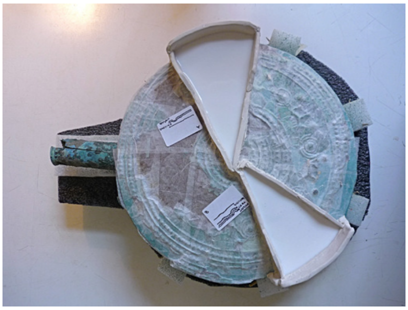


Fig. 14: Two tests for the creation of a cast.

This work proves that the analysis performed on findings before restoration in order to understand their nature and problems can contribute substantially to the choice of most appropriate treatment to be made.

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