

Survey of the Italian Archaeological Precious Metal Collections: Characterisation of the Patina and Study of the Degradation Phenomena

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To choose the correct strategy for the conservation of metallic archaeological artefacts, it is of importance to study the complex chemical-physical processes that occur during aging. The condition of the artefacts is the result of their intrinsic metallurgical features and environmental conditions, in which the metallic artefacts were buried and are now stored or exhibited. This study could help archaeologists and curators to find the history and the evolution through ages of the archaeological remains, and when feasible, to preserve, restore, protect and display them in museums without causing further damages.

Keywords: conservation, metallic artefacts, corrosion, burial, patina, portable equipments

1. INTRODUCTION

Among the metallic artefacts the precious ones are particularly interesting from an historical, artistic and economical point of view because they have been used not only as jewels or artistic items but also for currency, medium of exchange and form of saving. The precious metal artefacts are characterised by a wide compositional range (Ag, Ag-based alloys, Au, Au-based alloys, Ag and Au coated artefacts) and by complex manufacturing techniques that can influence noticeably their chemical and metallurgical stability. Furthermore, in these alloys different amount of impurities coming from extractive or refining processes such as Cu, Pb or Bi may be present and influence the long-term mechanical and chemical properties.

Dealing with the conservation state, the ancient precious artefacts are often fragile and are subjected to various corrosion processes, notwithstanding the electrochemical nobility of the metals involved. Silver and silver-based alloys are unable to form a stable protective surface film [1-4]. Depending on the environment, a thin layer may grow on the surface of these alloys reflecting the metal and insoluble corrosion products such as Ag₂S, AgCl₂, CuO, Cu₂O, Pb- or Cu-carbonates mixed to form a complex composite structure. If silver is exposed specifically to environments containing sulphur compounds the well-known tarnishing phenomenon takes place and ageing phenomena can also occur in silver-based alloys. The gold-based or nearly pure gold artefacts are more stable with respect to the silver artefacts, however they are exposed to deterioration for example in the areas where joining or severe thermo-mechanical treatments have been carried out in order to produce very thin sheets. Moreover, the less noble metals pre-

sent as traces or alloying elements such as Pb, Cu and Bi, can have a detrimental effect on the chemical and physical stability of the precious metal artefacts due to the formation during casting, thermo-mechanical treatments or ageing, of separated metal islands or secondary precipitated phases. The resulting alloy, whose equilibrium state is not a single phase, is less resistant to long-term corrosion; as a matter of fact during burial or atmospheric exposure, porosity, cellular precipitation, interdendritic pores, cracks, depleted areas can be generated.

More complex degradation phenomena are found with Ag or Au coated artefacts produced via gilding or silvering as well as for immersion in melted metals or via mechanical adhesion and diffusion thermal treatments. As a matter of fact, the corrosion behaviour is dramatically affected by the intimate contact between metals with different electrochemical potential, Ag and/or Au of the external layer and Cu or Cu-based alloys of the bulk: as well-known this contact induces accelerated corrosion in the less noble anodic areas.

The development of tailored conservation strategies for these ancient metallic artefacts needs the understanding of the complex chemical and physical processes that occur on them as a function of the surrounding environment, soil, water or air [5-7].

For this reason, a survey was carried out of the Italian archaeological precious metal collections with the use of different analytical techniques, and when possible with portable instruments.

In this paper some artefacts coming from the collections of the Archaeological Museum of Sant'Antioco (Sardinia, Italy), that constitute the most important exhibition of the Phoenician-Punic culture in the Mediterranean Basin, are studied. In Fig. 1 an exhibition room is shown.

Survey of the Italian archaeological precious metal collections



Figure 1 - Archaeological Museum of Sant'Antioco.

The collections, enriched by the archaeological excavations carried out in the last centuries and by occasional findings include 15.000 archaeological artefacts: jewels, coins, weapons, amulets, gems, mosaics, glasses, common use objects, large bronze and marble statues, reconstructions of tombs of the V century AD. Of particular interest, the big statues of two lions in tufaceous materials, positioned at the sides of the door of the ancient Sant'Antioco, named Sulky, and dated back to V and IV century AD., Fig.2.

It is worth noting that the metallic artefacts collections in particular are constituted by more than 1.000 gold, silver and copper based artefacts.

Some representative jewels, cups and coins have been selected for the study after examining several silver or gold-based archaeological artefacts of Phoenician-Punic and Roman periods and/or fragments of them.

The artefacts, selected for their technological and artistic relevance and representative of the whole collection, are important from a historical point of view because they are objects produced by using precious metals and represent the witnesses of the ancient economy and of the art.

The conservation state and the general exposure condition of the items are in some cases very good; only few coins and artefacts are characterised by heavy degradation phenomena induced by soil constituents attack and chloride and sulphide corrosion. The more precious items are stored in showcases where the environmental parameters are continuously controlled. The other artefacts are stored in polyethylene containers avoiding any contamination and pollution as well as post-burial degradation.



Figure 2 - Lion statues of the Archaeological Museum of Sant'Antioco.

Only archaeological artefacts that have never been restored or subjected to any conservation treatment have been considered in this study in order to better identify the degradation phenomena. The only treatment needed was cleaning, in order to remove raw encrustations and soils relics.

2. EXPERIMENTAL

The investigation aimed to identify the chemical composition of the bulk material and to ascertain the morphology and the chemical composition of the corrosion layers present on the artefacts.

Different analytical techniques have been used: *in-situ* Optical Microscopy (OM), Scanning Electron Microscopy (SEM) and X-ray Diffraction (XRD). The experimental apparatus that have been employed are: portable Leica microscopes equipped with digital cameras, FEG-SEM-EDS Leo 1530, SEM-EDS Cambridge 360, XRD diffractometer Seifert D3000. The conditions of the analysis were non-invasive or in some cases micro-destructive.

As a matter of fact, non-destructive techniques are important tools for conservators to obtain information about the conservation state of artefacts, moreover, the possibility of performing the characterisation *in-situ*, without transferring the artefacts from the museum to the laboratory can reduce further damages [8]. In particular, this study is a successful application of a portable optical microscope for the *in-situ* characterization of precious ancient artefacts in the museum.

3. RESULTS AND DISCUSSION

3.1 Gold and gold-plated artefacts

All the gold artefacts have been found in good conservation conditions. As an example in Fig.3 a gold earring produced by means of different manufacturing techniques, including casting, joining, twisting and heat hammering, is shown.

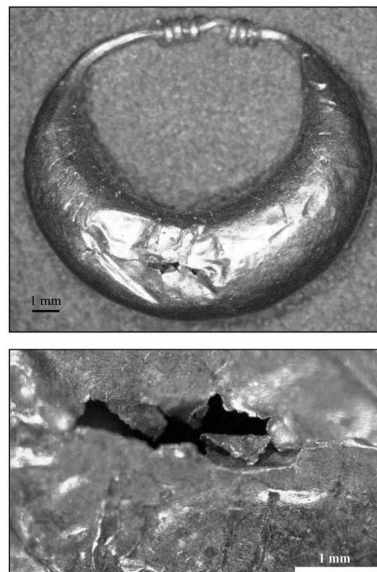


Figure 3 Optical micrograph of a gold earring (top) with the enlargement of the cracked area (bottom).

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A softened (by heat) wire has been partially beaten to obtain a thin sheet and also shaped for producing the required dimensions. The conservation state of the earring is good notwithstanding the cracks in the thinner areas of the central part. Probably the metal has been overheated thus inducing brittleness and causing susceptibility to crack with ageing. Because of the absence of surface corrosion phenomena, no chemical treatment has been applied, only washing with water and gentle cleaning from the soil components.

On the other gold artefacts no surface degradation phenomena has been evidenced, while the observed susceptibility to cracks with ageing has been related to metal overheating that induces brittleness. The gold artefacts are not corroded but only brittle, so they do not need any protection: the only recommendation is to avoid incorrect manipulations that can cause mechanical stresses.

On the contrary, the gold plated artefacts show severe corrosion problems, as the gold plated silver earring and the gold plated brooches for braid of hair respectively shown in Figs. 4 and 5.



Figure 4 - Optical micrograph of a gold plated silver leech-shaped earring (top) with the enlargement of the cracked area (bottom).

The gold plated silver earring with the so called shape “leech” of Figure 4 shows noticeable degradation processes that took place from the interior constituted by silver. The artifact is fragmented and extremely brittle as a consequence of the occurrence of galvanic corrosion phenomena with silver acting as anode of the couple. Furthermore

the presence of chlorides in the environment leads to the presence of noteworthy amounts of chloroargyrite in the corrosion products as detected by XRD analysis.

The gold plated brooches of Figure 5 show similar problems of corrosion, as a matter of fact they are cracked in some areas with the exposure of the copper substrate covered by corrosion products. In particular, on these artefacts the presence of noticeable amounts of paratacamite was detected by XRD. Galvanic corrosion phenomena associated with the ubiquitous presence of chlorides lead to the precipitation of these corrosion products.



Figure 5 - Optical micrograph of gold plated brooches for braid of hair (top) with the enlargement of a cracked area of the artifact on the left (bottom).

3.2 Silver and silver-plated artefacts

Some of the silver artefacts exposed have been found fragmented already during the archaeological excavations; these artefacts are in an extremely brittle condition being easily broken with a little stress and a small deformation. Even though the artefacts show signs of external corrosion, this is not the only cause of brittleness that can be also attributed to ageing phenomena. It is worth noting, that silver should have been quite ductile when the artefacts were produced and a time dependent mechanism has modified the metallurgical properties thus inducing brittleness. This is the case of the silver bracelets shown in Figure 6.

The optical images of the cross-section of a fragment clearly show the inter-granular nature of the fracture surface of the silver bracelet and the presence of small cuprite inclusions dispersed in the silver matrix.

The micro-chemical and micro-morphological analysis of the external corrosion products of the bracelets are constituted mainly by chloroargyrite (AgCl) and di-

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genite (Cu_9S_5) as shown in the XRD diffractogram of Figure 7.

Silver-plated artefacts are characterised by complex degradation phenomena.

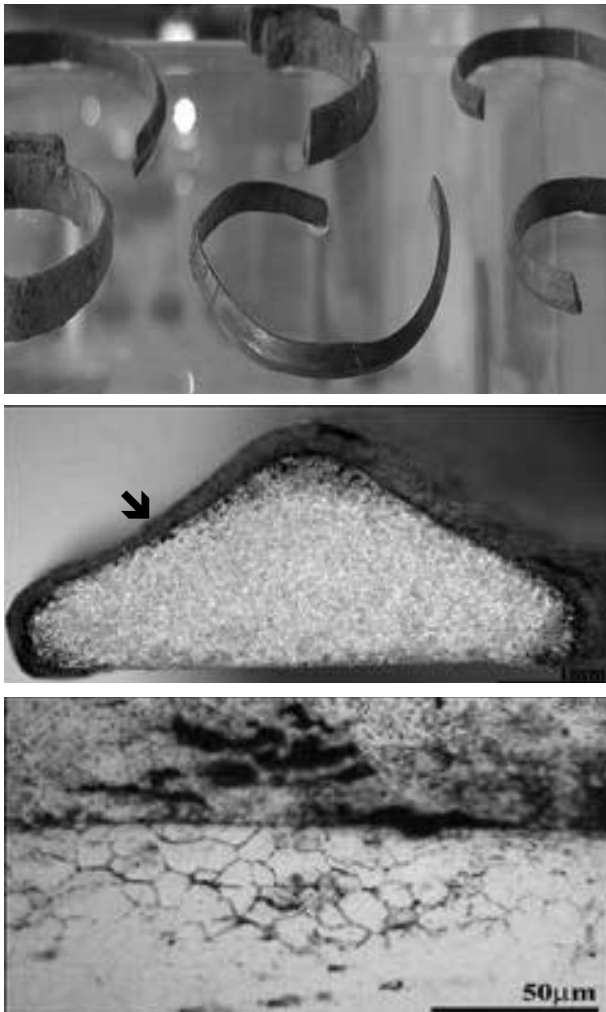


Figure 6 - Carthaginian silver bracelets (top), optical images of the cross-section of a fragment (middle) and enlargement of the indicated area (bottom).

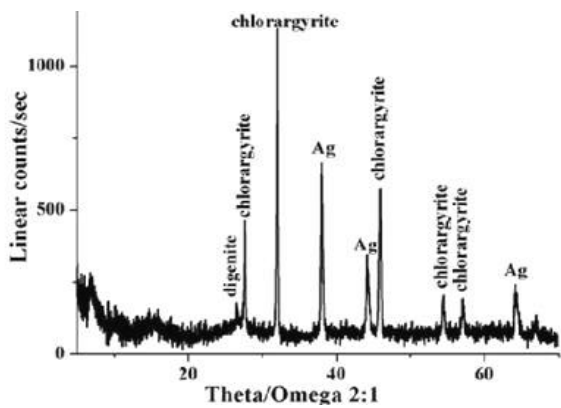


Figure 7 - X-ray diffractogram of the corrosion products of the Carthaginian silver bracelets

The ring shown in Fig. 8, is constituted by a copper substrate plated by a layer of silver. The chemical composition of the alloy used for plating the copper substrate is Ag 91.3, Cu 7.3, Pb 0.70 (wt %). The artefact is fractured in the welded regions and presents the occurrence of bronze disease in the copper enriched areas.

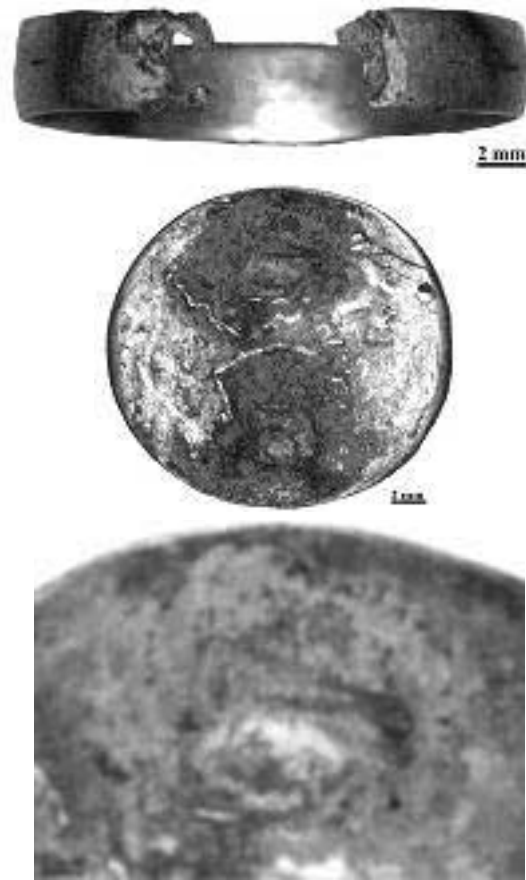


Figure 8 - Silver-plated ring produced by soldering a ring (top) and a setting (middle), enlargement of the corroded area (bottom).

4. CONSERVATION STRATEGY

The *in-situ* OM observations of the gold artefacts exhibited in the Archaeological Museum of S. Antioco confirm their good conservation state. At present, no protection treatment is required. However, a preventive conservation procedure in showcases may be useful in order to control the environment by using exhibition showcases with inert gases inside and the use of activated charcoal filters and silica gel.

On the contrary, the survey, by OM and the other analytical techniques of gold-plated, silver and silver-plated artefacts indicated that the degradation is mainly due to the presence galvanic corrosion phenomena combined with the action of chloride ions coming from the environment. The preventive conservation procedure in these cases could be the removal of chlorides and the utilisation of

inhibiting and protective coatings to ensure a long-term chemical-physical stability to the artefacts and to stop the degradation of the copper islands present in the silver-based alloys [9,13]. Interesting results have been obtained with PECVD SiO_x-like coatings that show excellent barrier properties against aggressive agents and look really promising for the protection of silver-based alloys artefacts against tarnishing [10].

5. CONCLUDING REMARKS

The adopted multidisciplinary approach to the survey of the collection of Archaeological Museum of S. Antioco performed in cooperation with the Director of the Museum, an archaeologist, and conservators, may help them to find the history and the evolution through ages of the archaeological remains and, when feasible, to preserve, restore, protect them without causing further damages.

Furthermore, the possibility to employ portable instruments is very successful in helping to answer specific questions concerning conservation aspects and for investigating degradation phenomena of precious ancient artefacts. From here, it is possible to choose the most suitable environmental conditions for the storage and exhibition of these artefacts.

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