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ARCHAEOMETALLURGICAL CHARACTERISATION OF COPPER-BASED ARTEFACTS

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Abstract

Since Romans generalized the use of brass, an copper and zinc alloy, it could replace bronze, an alloy of copper and tin, particularly in localities where bronze production was restricted due to tin shortage. According to the ternary copper–zinc–tin phase diagram, the addition of tin to brass lowers the liquidus temperature and considerably increases the freezing range. The ternary phase diagram also predicts the precipitation of the eutectoid at relatively lower tin contents in the presence of zinc.

Key words: *copper artefacts, archaeometallurgy*

1.INTRODUCTION

From prehistory till nowadays, the modification of metal object surface is an important technological process used to improve properties of the basic material.

A new scientific field, which combines the technologies of many disciplines, has progressively grown in importance: Archaeometry. And it should be pointed out that the relevance of the contribution of Science for the overall knowledge and for the conservation of the Cultural Heritage is widely acknowledged by the community of 'humanists' themselves.

Historical documents on the early metallurgical processes are scarce, and they satisfactorily describe technical details only starting from the modern age. Universally acknowledged sources for post-renaissance metallurgy are Georgius Agricola's "De re metallica" (1556) [1] and Vannoccio Biringuccio's "De la pirotechnia" (1540) [2]. Direct information onmetallurgical techniques in previous historical times are gathered from fragmentary and incomplete texts or graphical representations (Egyptian hieroglyphics,Near Eastern cuneiform tablets, Roman trade or mining regulations, Pliny's comments, etc.) [3, 4].

For prehistoric times there is no direct information, so that knowledge on the extraction diffusion and use of metals in antiquity has to be derived from archaeological and archaeometric investigations [5–7]. In general, the interpretation of the origin and the diffusion of minerals, metals and artefacts relies on information provided by elemental or isotopic analysis, whereas the reconstruction of the technical details of the metallurgical processes, such as smelting, roasting, slagging, alloying, casting, etc., mainly relies on information obtained by techniques of physical or mineralogical characterization. Recently, the systematic application to ancient metals of advanced techniques developed for the characterization of modern industrial materials is producing a remarkable advancement in

archaeometallurgical knowledge. Ever since the Romans generalized the use of brass [3], an alloy of copper and zinc, it could replace bronze, an alloy of copper and tin, particularly in localities where bronze production was restricted due to tin shortage.

Conservation of metallic objects belonging to our cultural heritage is an open field in corrosion research [5]. For that purpose, the knowledge of corrosion processes is required, especially when the equilibrium reached along centuries by the metal and its corrosion layer is broken. Many factors can influence the reactivity of ancient metals:

-Excavation of buried artefact exposes the object to a variation of oxygen pressure, as oxygen in deep geological layers is considered to be absent

- Outdoor exposure to rainfall in urban environment creates highly acidic conditions, at least for the first drops or during drying.

- Indoor exposure, even in museums, generally considered as safe places, concentrates organics pollutants.

2. EXPERIMENTAL

This study will show two examples of corrosion products on metal artefacts. The first example will show the analysis of some corroded bronze objects. The second example deals with alloy corrosion on Romanian coins. The surface morphology and chemical composition as well as the micro-chemical structure of the corrosion products grown on the artefacts were studied by means of the combined use of optical microscopy (OM), X-ray diffraction (XRD) and energy dispersive X-ray fluoresence (EDXRF).

3. RESULTS AND DISSCUSION

As seen in our previous reports [6-9] in the archaeometallurgical characterisation of copper based artefacts, some aspects must be considered:

(1) corrosion studies;

(2) studies on the technology and authenticity

(3) the origin and provenience

The type and the chemical evaluation of the corrosion products that appear depend on the nature of the substrate and the environment in which the artefacts was found. The patina chemical and structural features may be influenced by different corrosion mechanisms that in some cases give rise to the formation of unusual corrosion products or alternated stratified layers. In the literature [10,11], the corrosion products are correlated with the environment in which the artefacts were found: the highest air pollution levels are usually associated with the occurrence of thick, black or dark grey corrosion layers on copper or bronze objects, preferentially containing soot, iron oxide hydroxides, and antlerite, $Cu_3(SO_4)(OH)_4$. Pale green corrosion usually contain brochantite, $Cu_4(SO_4)(OH)_6$, and is rather associated with less polluted areas. Atacamite, a copper hydroxide chloride with the chemical formula $Cu_2Cl(OH)_3$, is preferentially observed in coastal regions.

3.1 Bronze artefacts – roman mirror

In the roman mirror, copper is the main element in the alloy, and the lead is present in less than 10%. Tin is present on a concentration of aprox. 20%. The XRD analysis revealed the intermetallic alloys such as $Cu_{81}Sn_{22}$ and $Cu_{5,6}Sn$ and also the presence of lead. With the help of optical microscopy, the corrosion products present at the surface of the mirror were analysed, confirming the presence of cuprit and cuprous chlorides.

The elemental composition obtained by XRF can be used in more ways:

- fast and reliable determination of the alloys composition;

- provenance – trace-elements could indicate the provenance of the ore or of the alloy;

- conservation – some protecting measures could be adopted based on the composition;

- restoration – the elemental composition is needed in order to use similar or compatible materials;

- historical studies – based on the results, some conclusions can be drawn regarding the technologies used and the commercial relationships.

3.2 Romanian coins

For the Romanian coins study, was followed the chemical composition of the alloys, the corrosion products that appear, as well as the correlation chemical composition-historic age.

With the help of XRF, the coins studied could be divided in three categories:

- Ag/Cu alloys

- Cu/Zn alloys

- Cu/Sn alloys, where Zn is present

The results obtained for the samples are shown in Table 1, for the major elements; traces of minor elements were also found (Co, Ni, Pb, S and others).

The results can be easily correlated with the ages in which they were manufactured (those containing silver – in 1900 – the age of the 'gold leu' and 1944 – a period of World War II in which precious metals were used for manufacturing coins; in the second case silver was probably used also due to it's great value - 500 lei. The coins from 1867 (the beginning of the coinage in Romania), 1930 (a period of economic depression) all being also of small value, and 1945 (even if it represents a great value it was made in period at the end of World War II, a difficult economic time for Romania) were made from non-precious metals.

Table 1. The coins' composition determined by EDXRF.

Coin	Element (%)				
	Fe	Cu	Ag	Zn	Sn
#1	0.15	12.60	86.25	-	-
#2	0.25	75.5	-	22.25	-
#3	-	12.25	84.0	-	-
#4	0.35	64.0	-	35.50	-
#5	0.29	84.2	-	1.3	5.99
#6	0.29	86.8	-	7.54	-

3.3 Corrosion products

By the surface morphological features observed via optical microscopy (figure 1) we can see the presence of what we suppose to be copper corrosion products such as cuprite and chloro-argyrite (supposition based on the chlorine detection by a semi-quantitative XRF analysis, and by classical analytical methods).

In the corrosion of copper in soil (and also atmospheric environments), the first product to form is cuprite. In the presence of S in the environment, the formation of sulfates and oxysulfates is favoured and these phases are generally found above the copper oxide-containing layer.

According to E-pH diagrams for copper [12], the reduction of cuprite to copper begins when the oxidising potential and /or pH drops. The oxidising potential decreases from the surface towards the core of the objects because of both the consumption of oxygen in the oxidation processes on the surface and the presence of corrosion layers.

The corrosion product structure consists largely of copper oxide (Cu_2O). The presence of cuprite (Cu2O) is due to selective corrosion of the main alloying element, which is redeposited after dissolution onto the surface of the silver coin, thus forming a copper enriched layer. Furthermore, some cracks are present along the patina as a result of volume changes upon corrosion, which enhances the diffusion of soil elements from the soil to the inner areas of the coin.

In the copper/silver alloys, the results shows evidence of the presence of silverchlorine species, likely chloroargyrite (figure 2), and copper-chlorine compounds on the silver coin surface as well as the active localised corrosion phenomenon commonly defined as “bronze disease” [13].

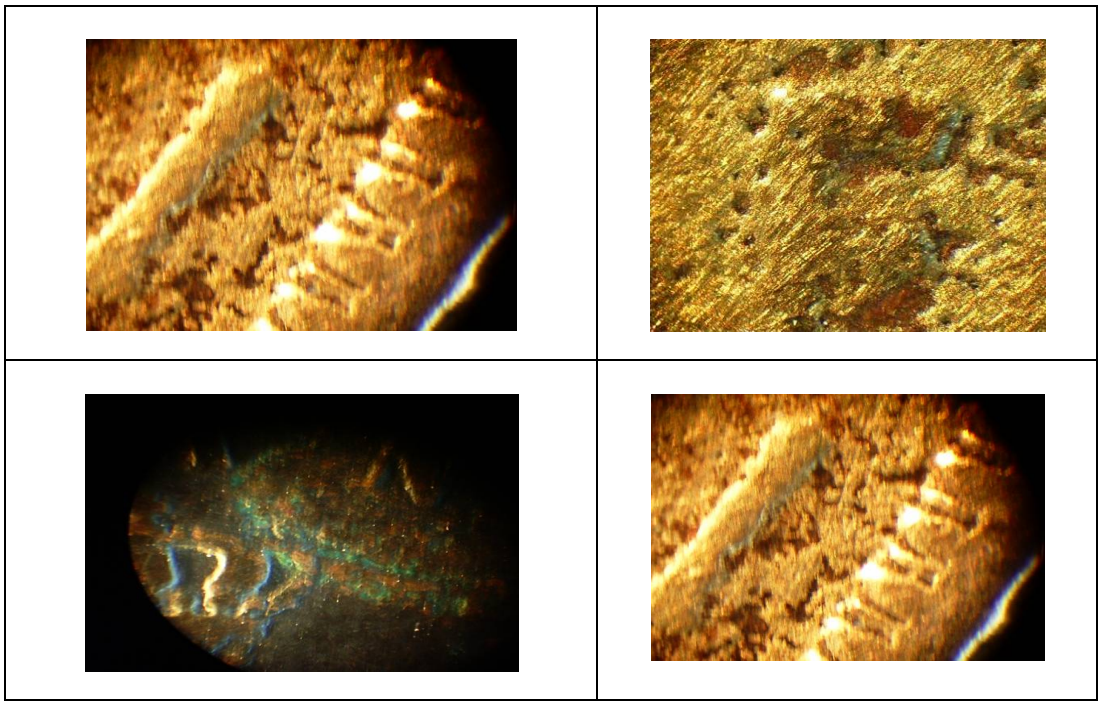


Figure 1. Surface morphological features observed via optical microscopy

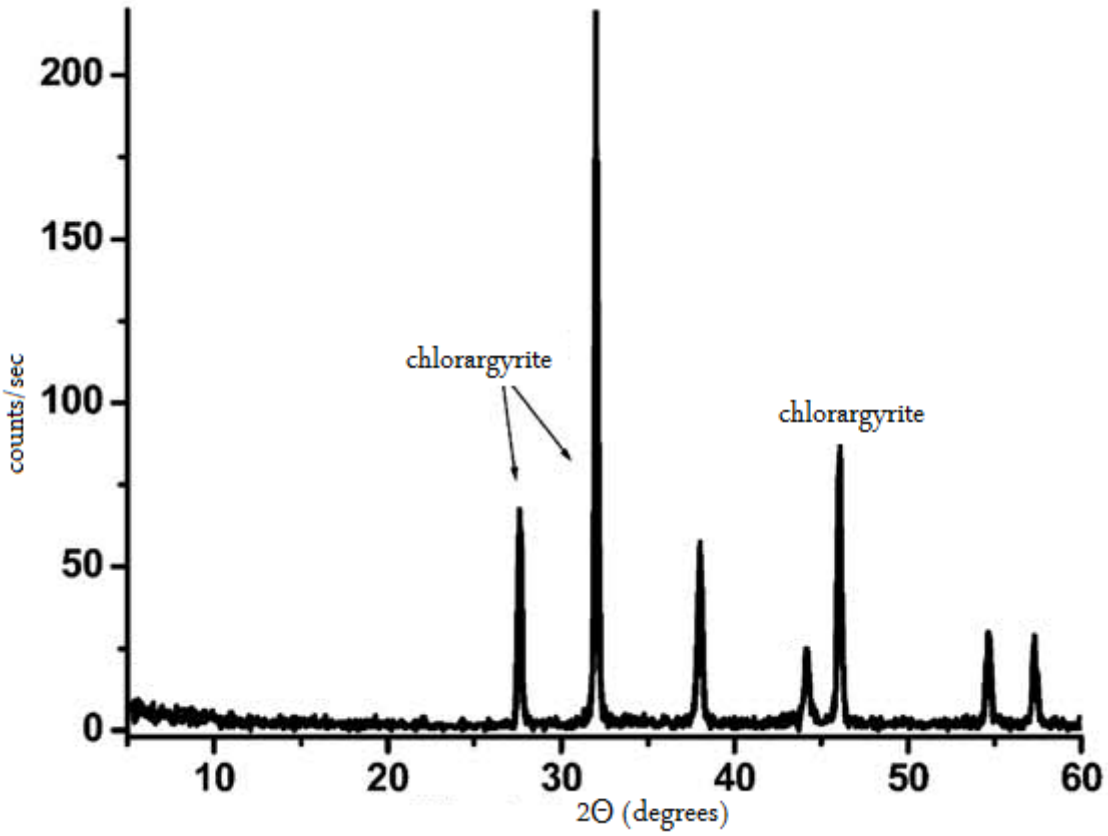


Figure 2. XRD diffraction pattern of chloro-argyrite

As a consequence of the intimate contact between copper and silver which have different electrochemical potentials, corrosion phenomena are induced on a microscopic scale. Indeed, the contact induces the less noble metal to become anodic in a couple strongly conductive to corrosion, and a preferential dissolution of copper occurs in the less noble anodic areas. The amount of current that flows, and therefore, the extent of the corrosion, is subject to many variables, among which are the chemical-physical parameters of the burial context, the presence and nature of the electrolyte, and the micro-chemical structure of the alloy.

This latter cyclic reaction occurs in the copper enriched areas and is induced by cuprous chloride, oxygen and humidity. The presence of the copper islands in the silver alloys is a common feature of the silver-copper alloys due to the low solubility of Ag in Cu and vice versa at room temperature (r.t.) [14,15]. Indeed, the solubility of copper in silver is about 8–10 wt% at 780 ◦C (eutectic temperature) and practically nil at room temperature (r.t.). Therefore, during the solidification in the copper-silver system, each component separates into a nearly pure state and has the same crystal lattice as the respective supersaturated solid solution. As a consequence, dispersed copper islands are formed in the silver matrix whose size is influenced by the cooling parameters [14,15].

As a consequence of the intimate contact between copper and silver which have different electrochemical potentials, corrosion phenomena are induced on a microscopic scale. Indeed, the contact induces the less noble metal to become anodic in a couple strongly conductive to corrosion, and a preferential dissolution of copper occurs in the less noble anodic areas. The amount of current that flows, and therefore, the extent of the corrosion, is subject to many variables, among which are

the chemical-physical parameters of the burial context, the presence and nature of the electrolyte, and the micro-chemical structure of the alloy. These factors can induce the selective corrosion phenomena of copper by chlorine due to the cyclic reaction that is commonly defined as bronze disease. Chlorine also corrodes silver during the archaeological burial in the soil

4. CONCLUSION

The combined use of OM, XRD and EDRXF analytical techniques have provided good insight into the bulk nature and surface corrosion products grown on the atefacts analysed during archaeological burial. OM, XRD and EDRXF results indicate on the surface damaged areas the presence of chlorine as an aggressive agent as well as giving evidence of the chemical reaction between some soil constituents Cl, Mg, Al, Si, Fe, Ca) and degradation products. In addition, SEM-EDS, OM and XRD results show the occurrence of selective localised or general chlorine corrosion phenomena induced also by the separation of the alloying elements, which creates reactive electrochemical areas.

Finally, the chemical composition, the micro-chemical structures and the metallurgical features of the artefacts have been determined and can be used to identify some technological aspects of the ancient manufacturing processes. This information could be also used for producing Agbase reference alloys whose micro-chemical structure and chemical composition are similar to those of the ancient ones. These reference materials could be employed for carrying out accelerated degradation tests by simulating as best as possible, the specific corrosion conditions and the aggressive agents previously identified and then, to validate correctly the restoration and conservation procedures.

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