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MICRO-STRATIGRAPHY OF COPPER-BASED ARCHAEOLOGICAL OBJECTS: DESCRIPTION OF DEGRADATION MECHANISMS BY MEANS OF AN INTEGRATED APPROACH

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ABSTRACT
The aim of this paper is to presents preliminary results obtained during a study performed on artifacts made of copper-based alloys in two archaeological sites in Dobrogea, Romania (the two villages of Nufărul and Ibida). An integrated approach makes use of OM, SEM-EDX, XRD, FTIR and RAMAN spectroscopy both on surface and polished cross section and revealed the complex multilayered structure of the alteration layers.

INTRODUCTION
Degradation of metal artefacts in soil occurs through different processes: chemical, electrochemical and microbiological. As a result, they tend to return to their mineral's state, as thermodynamically more stable then the metallic state. The way this processes occur is a function of multiple factors that can be classified as endogenous (nature of alloy, technology to obtain the object, its shape and dimension) and exogenous (soil porosity, humidity, conductibility, depth of burial…) [1].

As early as in 1976, a polish chemist, Hanna Jedrzejewska [2], suggested to consider ancient bronzes as "document of the past" and proposed to preserve materials of little or no artistic value for scientific investigations. Since that time, several Authors [3-8] dedicate their scientific interest to the elucidation of the long-term corrosion mechanisms occurring for artifact made of bronze or copper alloys.

A comprehensive study realized by Mattsson *et.al.* [8], focused on the enhancement of degradation observed in the last decades because of the acidification of rains. In particular they tried to establish a correlation between the alteration suffered by bronze artifacts, their actual environment (geology, geography, local or distance from polluting sources) and their archaeological context (type of site, depth of burying), by visually examining the degree of degradation, measuring the weight of the artifact and determining numerous parameters characterizing the objects (chemical-physical data records).

The present work intends to give our contribution in the understanding of the mechanisms of degradation by presenting the results obtained during the examination of heavily degraded copper-based artifacts excavated in two archaeological sites located in Dobrogea, Romania. The purpose is to report the occurrence of uncommon alteration products interesting degradation patterns, and to delineate a research project that involves a campaign of analyzes aimed to characterize the soil of the archaeological sites described later in detail. These information could be useful not only to give a better interpretation to the results already obtained, but also for any further investigation undertaken for artifacts excavated from those sites.

PROJECT OVERVIEW

This research is carried out in the framework of the EU-funded project EPISCON, European PhD in Science for Conservation, through the Program Marie Curie EST-FP6. This work is part of a PhD, which involves studying of the climate parameter of the archaeological site through the history and gathering general information about the geology of the archaeological sites considered. Physical-chemical analysis and micro-morphological characterization of the soil will be performed.

EXPERIMENTAL PART

Samples

Small finds made of copper-based alloy are very commonly found by archaeologists. Some of them have little or no historical value, but, on the contrary, they represent a source of precious information for a scientist. The analytical results obtained during the investigation of three objects (Table 1), are here disucssed. They were found in two important archaeological sites located in the region of Dobrogea (Romania): Nufarul and Ibida.

Archaeological Sites

Nufarul

It is a village located on the bank of one Channel of the Danube’s Mouth, an area intensely exploited for commercial traffic and navigation, as well as for natural resources, representing a strategic target for Byzance. Archaeological researches revealed, on the right side of the Sfantul Gheorghe Channel, the area of Nufarul of today, the existence of an important urban center from the X-XIV centuries, guarded by Byzantine fortifications built in the X-th century.

Seven copper coins fragments were founded in this location. As they were already sectioned, it has been possible to study the stratigraphy of the alteration layers just by polishing with SiC paper, without having to mount them with a polyester resin.

Ibida

Ibida is the largest late Roman city from Romania with a surface of 24 ha. and 30 towers. At south-east of this area, on a hill, the surveys have identified a smaller fortress, dated, after the materials found there, from the 6th c. AD; the archaeologists have supposed it was a last defending place in case of destruction of the city. On another side, researchers have revealed two construction phases, one from the end of the 4th c. AD, the other from the 5th c. AD, based on analysis of ceramics and coins founded in the site.

Sample	*Photo*	*Brief description*
Nu01		almost completely mineralized copper coin excavated in Nufarul
Nu03		completely mineralized copper coin excavated in Nufarul
Ib06_09		highly corroded hair stick (?) excavated in Ibida

Table 1

Methods and Analytical Techniques

A large-field examination of the corroded surfaces aimed to roughly estimate the degree of deterioration and to plan the micro sampling was undertaken both by naked eyes and with a stereomicroscope. Micro-samples have been withdrawn and mounted in a polyester resin to realize cross-sections (CS) by grinding and polishing according to the standard metallurgical procedures.

Observation by optical microscope, under dark field, allows a first characterization of the compounds present since they show a variety of colors and to get a first idea of their chemical composition. In this work an Olympus BX51M and a Leica DM 2500 M were used.

An integrated approach makes use of techniques that give both elemental and molecular information. In this study SEM-EDX, FTIR and Raman spectroscopy and XRD were available.

Scanning Electron Microscope coupled with an energy dispersive X-ray detector (SEM LSH II by Tescan; EDX by Bruker) was employed to determine the chemical nature of degradation layers by registering spectra in selected points, along a line (line scan) or over a larger area (mapping). The microscope is equipped with an electron gun with Tungsten filament and a gun potential of 30 kV was used for the measurements. The software Quantax QX2 was used to acquire the spectra.

Fourier transformed infrared spectroscopy allows the characterization of the functional groups of corrosion compounds which absorb in the region of mid-infrared (400-4000 cm^{-1}). A Thermo-Nicolet Avatar 370 was used in this study, the spectra was recorded in the transmittance mode with a resolution of 4 cm^{-1}. Micro-samples were taken by scratching mechanically the surface with a fine scalpel; the powder obtained was then mixed with KBr and pressed to realize a thin pellet.

Raman spectrometry and X-ray diffractometry were employed when the FTIR specroscopy failedas for example when it was needed to characterize oxides or sulfide, which do not absorb in the mid-infrared region. The instruments used are a Raman Spectrometer RPA HE532 equipped with an optic fiber, for non-contact measurements and a Diffractometer Bruker D8 ADVANCE. In the latter case, samples suitable for the XRD were obtained by scratching the surface, by grinding a tiny fragment in an agate mortar or directly on the surface of the object.

RESULTS AND DISCUSSION

Samples from Nufarul

As illustrated in the SEM images (Fig.1 and Fig.2), the two coins present different degradation patterns. In the first case (Fig.1), the solid metal core (copper, with lead inclusions) is still present, even if heavily corroded.

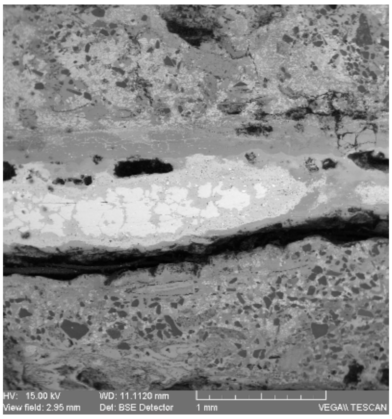


Fig. 1: Nu01_80x _BSE

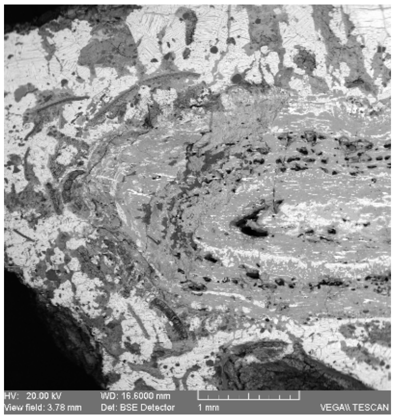


Fig 2: Nu03_60x_BSE

Microanalyses, performed with the EDS, revealed that high amount of chlorides (probably nantokite, CuCl) are located below the red layer of copper (I) oxide, cuprite. This confirms the role of the copper (I) oxide discussed by Lucey [9]: it has been considered acting as an electrolytical membrane allowing the transport of anions such as Cl^- and O^{2-} inward and cuprous ions outward. Indeed, the presence of copper chlorides in the archaeological artifacts indicates a noticeable transportation of chloride ions from the soil through the permeable alteration product layers to the internal zone and remaining Cu matrix.

The very thick degradation layer appears to be partly detached from the corroded metal core, and looks very compact. A number of point measurements have been realized in order to characterize this layer. EDS measurements, together with Cu, have detected elements like Si, Al, Fe, Ca, Mg, and Cl, thus demonstrating the very strong relationship that exists between soil constituent and degradation products.

A backscattered electron image registered for the other coin, Nu03, is shown in Fig. 3 The metal core here is not present anymore (Fig.3) and a layered structure is observed. In order to characterize these layers, an EDS line scan has been registered and the results are reported in the Fig.4.

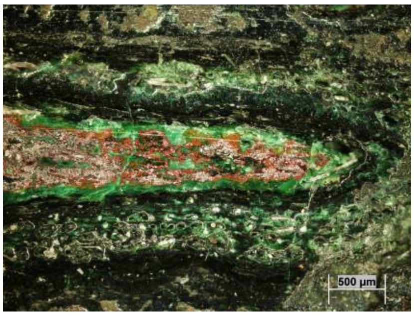
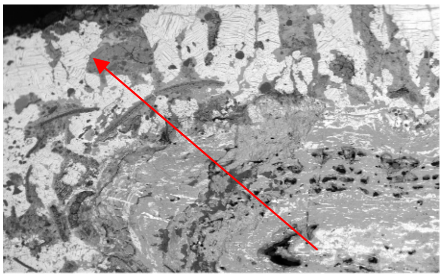


Fig. 3: section of the sample Nu03 by optical microscope, dark field, 50x.

As observed for the other coin, soil elements are detected in the outer layer, mainly Si, Al and Ca. The presence of Cu is higher in the core and, moving outwards, its trend follows the one of S, thus indicating the occurrence of a compound among them. A spectra has been registered by EDS on the wither areas of the external layer observed in the SEM image reported in Fig.4: it is reported in Fig.5 a.



SEM image_60x_BSE
(detail of the Fig. 2)

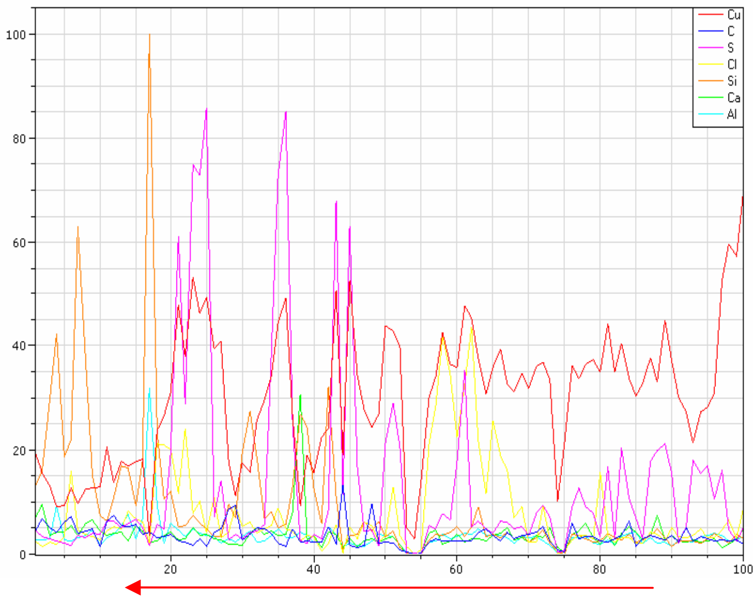
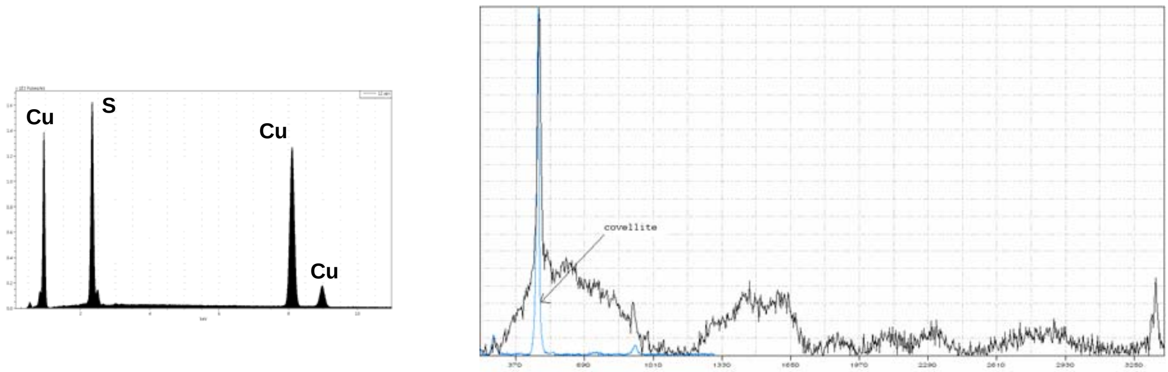


Fig. 4 : SEM-EDX elemental line scan: registered from the core to outer layers of the sample Nu03



a b

Fig. 5: EDX (a) and Raman (b) spectra registered on a point located the external layer of the sample Nu01.

In order to identify the compound, Raman spectroscopy was used due to its possibility to acquire a spectrum directly on the section by using optic fibers. The result is reported in Fig.5 b and reveals the presence of covellite (CuS) by comparison with a standard spectrum.

Sulfiding reactions are likely to occur in soil when sulfate-reducing bacteria (SRB) are present. Microbial consortia that include SRB produce anoxic, sulfide-rich environments in which the conversion of copper to copper sulfide is thermodynamically favored at a concentration of 10^{-2}M sulfide. Covellite is normally expected when an excess of sulfide is available [10].

Sample from Ibida

The picture in Fig. 6 shows the CS of a bronze (Cu-Sn) object, probably part of an hairstick. Subsequent thin layers of cuprite (Cu_2O), stannic oxide (SnO_2), constitute the very complex striated textured structure. The green compounds have been identified as malachite [$Cu_2(CO_3)(OH)_2$] and atacamite [$Cu_2(OH)_3Cl$].

Fig.6: microphotograph of the object Ib06_09 (OM). The polished cross-section shows the complex striated structure of subsequent layers of cuprite, stannic oxide and malachite. a. 50 x, b. 100x (metal core).

It is known [11] that a layer of cuprite grows on a copper alloy according to the metallic lattice parameter only until it reaches a thickness of 20 Å; afterwards, it follows the lattice parameters of its own. This results in structural strains that led to a mismatch and the film becomes porous. Moreover, the cuprous oxide (Cu_2O) can be considered an electrolytic membrane able to conduct ions through it. As a result, the oxygen and other compounds present in the environment come in contact with the metallic core and could interact with it according to the following electrochemical process (in presence of water):

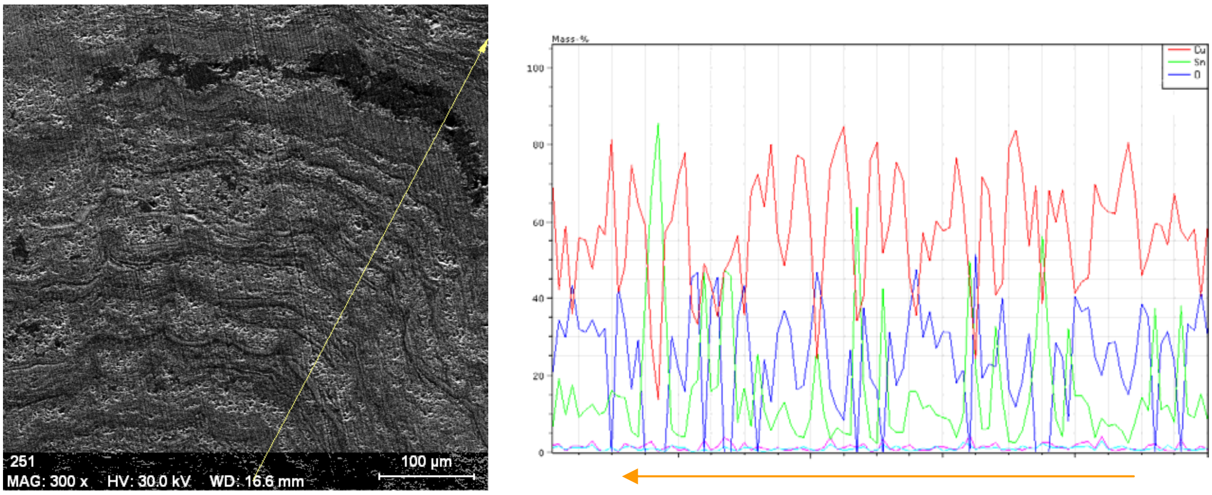
$$(-) \qquad Cu \rightarrow Cu^{2+} + 2e^-$$
$$(+) \qquad \tfrac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2\ HO^-$$

The increase of the pH led to the formation of azurite $Cu_3(CO_3)_2(OH)_2$ (thermodynamically less stable than malachite) or malachite, $Cu_2(CO_3)(OH)_2$.

The presence of tin in the alloy, and its reaction with oxygen, led to the formation of stannic oxide (SnO_2), which can form, by hydration, the stannic acid. At this point, the formerly produced, cuprite, tends to migrate to the environment as it is more soluble. The stannic acid, being immovable, maintains the initial form of the object and act as a chromatographic adsorbent, through which the carbonate and the oxide will advance.

Similar observations were published by Scott [4], who suggested that Liesegang phenomena may be responsible for the bended structure and presented an attempt of correlation between number and thickness of the layers.

Fig.7 shows the results obtained by SEM-EDX: acquiring a scan over a line allows the detection of the relative predominance of an element compared to others, hence to obtain information about their relative distribution on the selected line.



a **b**

Fig.7: microphotograph of the object Ib06_09, outer layer (SEM, Secondary Electron Image, 300x), a; and results of the line scan showing the relative concentration of Cu (red line), Sn (green line) and O (blue line), b.

In the figure above, it is interesting to notice the alterative occurrence of tin-containing (the green line in the figure) and Cu-containing (red line) compounds. XRD results confirm the presence of tin oxide and cuprite, besides malachite and atacamite.

CONCLUSIONS

The investigations undertaken evidenced the complex nature of degradation and deterioration of copper-based artifacts in soil. The results demonstrate the effectiveness of the integrated approach employed to study corroded archaeological artifacts.

Because of the low number of investigated samples and lack of information about the burial soil, general conclusion cannot be drawn and preliminary results are only reported.

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