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APPLICATIONS OF OPTICAL MICROSCOPY AND ENERGY-DISPERSIVE X-RAY SPECTROSCOPY IN THE STUDY OF A PENDANT FROM THE IIND -IIIRD CENTURY A.C.

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Abstract

Our paper presents the study of a basket-shaped pendant from the 2nd-3rd century A.C., discovered inside a funeral urn, in the Gabăra-Moldoveni necropolis, Neamţ county (Romania), in which we used optical microscopy (OM) and scanning electron microscopy, coupled with energy dispersive X-ray spectroscopy (SEM-EDX) The results of our experiments revealed that the corrosion crust contained complex, surface and interior structures. The exterior layer was relatively uniform, but the interior one was non-homogeneous, with a variable porosity. Those structures were generated under the anthropic influences, by burning rituals undergone before abandonment and under the influence of the environment in which the object was discovered, which triggered evolving processes of physical-structural and chemical deterioration. Their positioning, the morphology and the composition of the two structures (the surface and the area of contact with the basic alloy) were used to perform archaeometric evaluations.

Keywords: *Pendant; Funeral urn; Gilded silver; OM; SEM-EDX*

Introduction

Metallic artifacts resulted from surface investigation, or from archaeological digs, feature various states of conservation, in their internal and external structures, with overlapped corrosion layers, uniform or discontinuous, which allow us to detect certain archaeometric characteristics used in authentication and to explain certain aspects in regard to manufacture contexts, the abandonment and discovery of those artifacts [1-4].

Compared to copper alloys, which may feature a complex series of conservation states in the soil, silver alloys, especially the gilded ones, are usually well preserved. Whereas copper alloys rarely feature even, protective patinas that coat the metallic core - most of them are found with thick corrosion crusts, with or without a metallic core [1, 2, 5-9], concentric layers

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of the Liesegang type - the silver or gilded silver ones only feature contamination crusts from the archaeological site [10-14]. We know that the mode of formation and the position of the three types of chemical compounds (primary, secondary and tertiary), within the structures resulted during the underground stay of various metallic artifacts, are very important archaeometric characteristics used for authentication [15-19]. The three types of chemical compounds found in the primary, or noble patinas (formed during the manufacture and use period), secondary, or weak (formed during the abandonment period, or before that) and tertiary, or contamination patinas (formed during the underground stay period), are difficult to detect in silver and gold objects [15 - 19].

In interdisciplinary studies on the partial or general degradation of a metallic artifact in its corrosion crust, apart from establishing the limits of the corrosion layers by starting from the formation of chemical compounds and from the elements of physical deterioration (cracks, networks of cracks or pits etc.), one also focuses on the structures from the area of contact between the metallic core and the internal layer of the corrosion crust, that is, on the depth of the corrosion or the thickness of the corrosion crust and also on the size and morphology of the bulk [1, 3].

Generally, the processes of chemical alteration resulted from the interaction between the artifact and its environment are basically redox and complexation reactions, assisted acido-basically, but also a series of allotropic modifications, with structural-crystalline reformations. In order to elucidate the degradation mechanism during the underground stay, one takes into account a series of factors: the chemical composition of the basic alloy and the manufacturing technology of the artifact, its state of conservation before abandonment, its age, the physical-chemical and microbiological characteristics of the soil, the depth where it was found, as well as the anthropic influences before and after abandonment. Case studies on the conservation state of metallic artifacts, taking into account direct or indirect anthropic influences, offer diverse examples of transformations occurring during the underground stay [18-22]. Thus, objects found in incineration tombs, in cremation urns or pits, have complex structures, some atypical, with important characteristics that indicate the stages in the processes of chemical alteration and physical deterioration, whereas objects found at various depths in the soil, which were only affected by agricultural or industrial activities, do not contain such structures [23, 24].

Our paper presents a study on the conservation state of a pendant from the 2nd-3rd century A.C., made of gilded silver, that suffered a series of deformations and deteriorations under the influence of burning, before abandonment, during the funeral ritual, and which was subsequently deteriorated physically and chemically, during its underground stay. By using noninvasive techniques, such as OM and SEM-EDX, we analyzed the surface structures and the interference area with the metallic core of the basic alloy, intending to elucidate the nature of the materials and the technology used during the manufacture of the object.

Experimental Part

As a result of the archaeological researches performed in the Dacian-Carpathian necropolis Gabăra - Moldoveni, in Neamț county, Romania, in tomb 36, we discovered a gray ceramic urn (Fig. 1), which contained bone fragments and six silver items of jewelry, shaped as small baskets [25], with bone components and beads (Fig. 2) and the pendant under study (Fig.3).

Fig. 1. Urn with inventory number 5723:
a. after the intervention of preventive consolidation;
b. after final restoration

Fig. 2. Other objects contained in the urn

The pendant (Fig. 3) represents a small basket with three metallic pearls on its handle, almost equal in diameter. In the center of the four filigree rosettes (three on the edge of the pendant and one underneath - on its back), there are other four metallic pearls with the same diameter. The manufacture of that object involved a fine weaving technique, by using a thick circular thread, applied around the rosette and another, spiraled one, applied as a rosette holding the pearl and standing on the circular thread. The latter appeared to have been gilded.

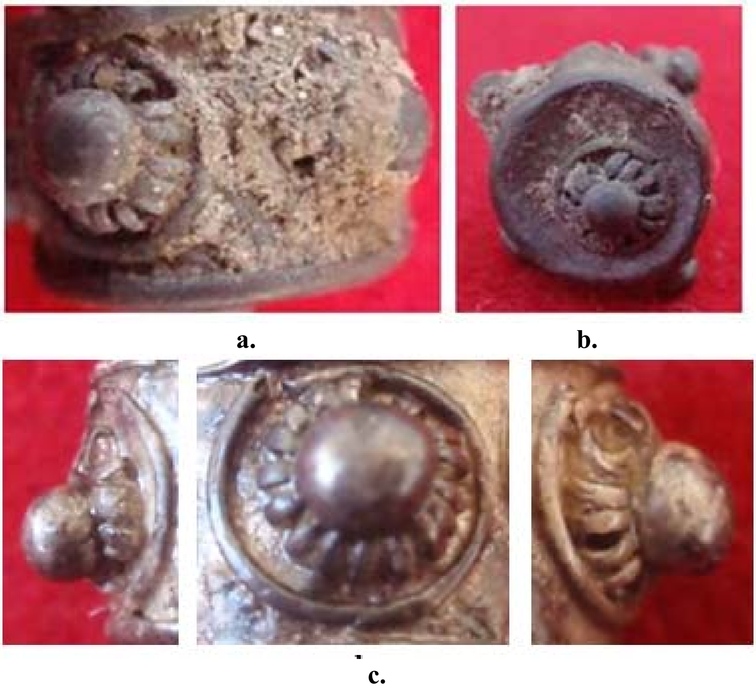
After extraction, the pendant was first subjected to some preliminary operations to clean the soil off it, by gentle brushing, followed by the removal of its superficial layer, by specific chemical treatments, suited to its structural type and to its composition. For preservation, they applied a thin layer of transparent varnish, by immersion.

Figure 3 presents the image of the pendant before and after restoration.

a. **b.**

Fig. 3. The pandant: a - before restoration, b - after restoration

In order to emphasize the preservation-restoration interventions, figure 4 presents details of the pendant, with images captured from different angles.



a. b.

c.

Fig. 4. Details of the pendant:
a. lateral view before restoration, b. bottom view before restoration
c. lateral ornaments after restoration and preservation

Under the crust with the contamination microstructures resulted from the soil, as a result of processes of semi-adherent monolithization, the gold coating featured a brown, aging patina that was interrupted by material losses in certain areas, which was blamed on wear, burning on incineration and on pedological processes from the underground stay period. The conservation state of the gold coating revealed that gilding was performed after the components of the item had been fixed together. What was unknown to us was the gilding technology used, because it was not plating.

Analysis Method

In our analyses, we used optical microscopy (OM), coupled with energy-dispersive X-ray spectroscopy (SEM-EDX)

The microstructures on the surface were studied under a Zeiss Imager A1m optical microscope, which was coupled with an AXIOCAM digital camera and by using dedicated software. In order to identify the chemical components and the positioning of the surface microstructures on the artifact, we used a VEGA II LSH microscope, made by TESCAN in the Czech Republic, coupled with a QUANTAX QX2 EDX detector, made by BRUKER/ROENTEC in Germany.

Results and Discussions

The pendant, which was unique in its shape and decorations among others within the collections of the History Museum in Roman (Romania), was particularly interesting for historians, due to the artistic and technique and the technology used for its manufacture. Its state of conservation was important, because it revealed the archaeometric characteristics formed during the manufacture, use and pre-abandonment periods, as well as from its underground stay period, as it was found in a closed environment (urn) and had come in contact with other materials [26-29]. In that regard, before cleaning, the object had a thin, relatively uniform, dark-brown layer, with contamination microstructures, its gold coating remaining hidden to eye inspection (Fig.5).

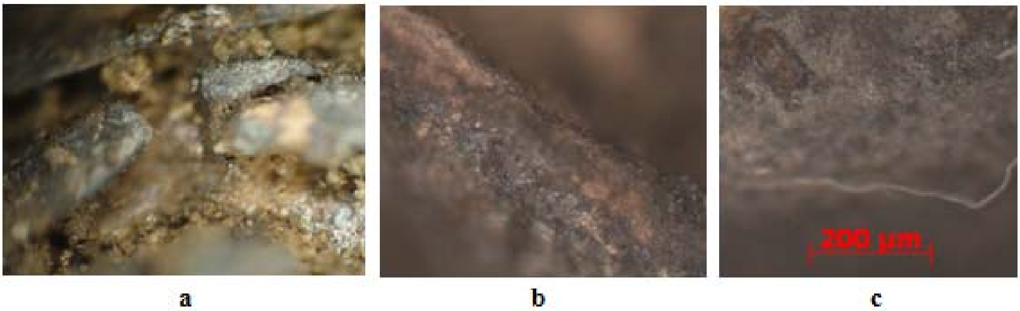


Fig. 5. Images of the surface layer: a - micro-fissures; b and c - microstructures of contamination

Our SEM-EDX analyses revealed the morphology and the composition of the external structures and of the area of interference between the corrosion crust and the surface of the metallic core of the pendant. In that regard, we found that the corrosion crust on one of the pearls had a porous structure with the following chemical elements: Ag, Cu, Si, S, Ca, P, Fe, Mg, Al and O (Table 1), according to the EDX spectrum shown in figure 6. The presence of Cu and Fe was assumed to be the result of microelements in its basic alloy, P and Ca were there by contamination with the bone next to which it was stored in the urn, Al, Mg and Si originated from the contamination microstructures in the soil and the S was presnt in the corrosion products, such as the silver sulfur which explained the dark color.

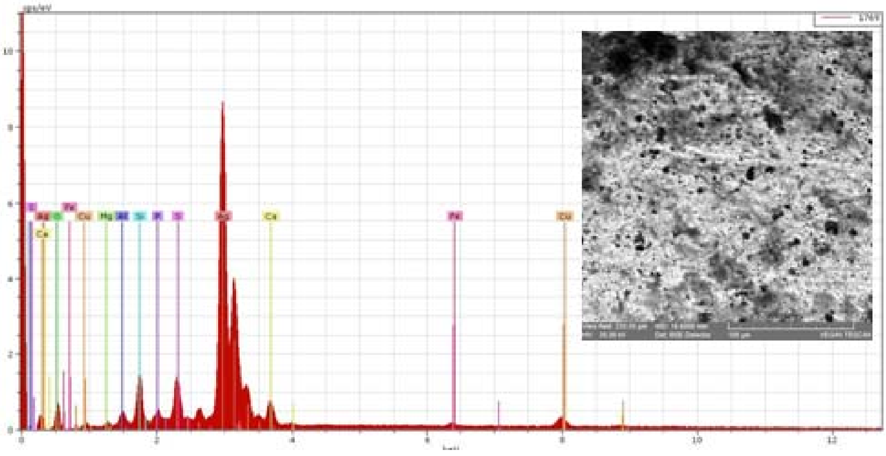


Fig. 6. The EDX spectrum of the pearl and the microphotogram of the corrosion layer at 1000x magnification with BSE detector

Table 1. Chemical components revealed by the EDX spectrum in Fig. 6.

Element	Weight, %	Atoms, %	Error, %
Silver	62.63297	25.39772	2.012946
Copper	2.721849	1,873528	0.102462
Iron	0.767413	0.601054	0.052269
Sulfur	3.845159	5.245102	0.172539
Calcium	3.624565	3.9558	0.143033
Phosphorus	1.23808	1.748394	0.081161
Silicon	4.903511	7.636764	0.250642
Aluminum	1.440253	2.334836	0.106532
Magnesium	0.280348	0.504528	0.050279
Oxygen	18.54585	50.70227	3.245316
	100	100	

In Figure 7 we present other structural areas of the item, from the exterior and also from the interface between the metallic core and the corrosion layers of the pendant. The corrosion layers were porous, with gaps, pits and fissures.

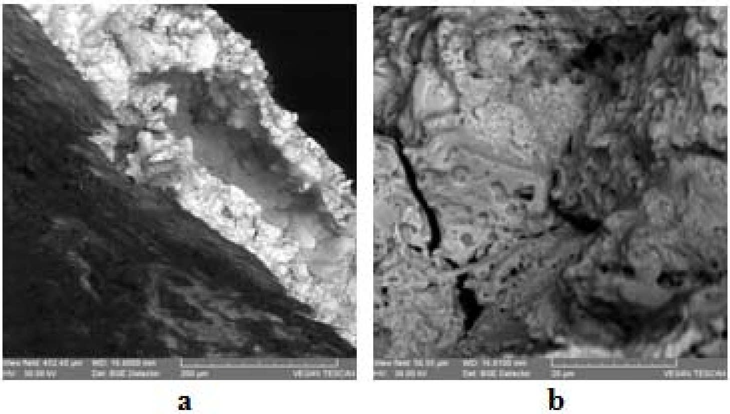


Fig. 7. Structural images of the pendant made by a BSE detector:
a. 500X magnification, b. 4000X magnification

The chemical components revealed by the EDX spectrum in Fig. 8 indicated the presence of Au, together with Ag and Cu, as the basic components of the alloy used in manufacture. The presence of gold was attributed to the application of gilding, a layer which was lost in time, due to certain successive processes, such as: wear before abandonment, burning during the incineration ritual and the degradation/deterioration processes that occurred during the underground stay period. Cl and Al originated from the contamination microstructures (Table 2). The thickness and distribution of the gold layer on the structural components of the pendant (pearls, thread and the body of the item) indicated that the gilding technique used was not plating, but immersion in molten metal (most plausibly), amalgamation with a liquid alloy of mercury and gold, or by rubbing the metal together with heated gold ore powder, chalk powder and charcoal, in the presence of some additives from plants (such as oak tannin) [9-13].

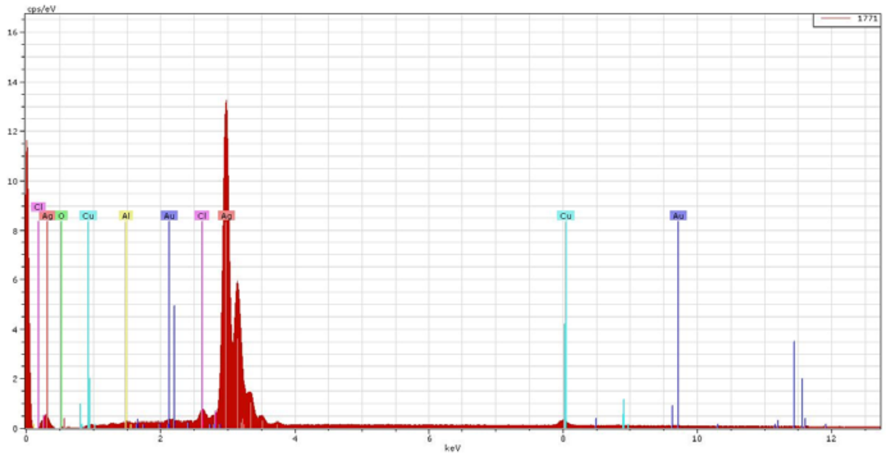


Fig. 8. EDX spectrum of the area presented in Fig. 7b

Table 2. Chemical composition of the area presented in Figure 7b

Element	Weight, %	Atoms, %	Error, %
Silver	93.62538	90.76601	3.373016
Copper	2.636346	4.338469	0.105284
Gold	2.857894	1.517316	0.119868
Chlorine	0.036628	0.10804	0.052892
Aluminium	0.84375	3.270162	0.080145
	100	100	

Conclusions

The pendant under study, due to its state of conservation, which deteriorated in time during its use, was subjected to thermal processes during the incineration ritual and the underground stay inside the urn (closed environment with a pedologically induced cryptoclimate) and featured a particular series of archaeometric characteristics. They were different from those found in general cases of artifacts from the same material and age, but which were found during archaeological surface inspections, or in soil, with or without incineration, with or without cryptolimate. Taking into account the composition of the basic alloy, together with the morphology, composition and the structures of the corrosion layers and of the gold coating, we concluded that the item was made by using the filigree technique and that its gilding was done by immersing it into molten gold.

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