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A STUDY ON SPECIFIC ARCHAEOMETRIC CHARACTERISTICS OF GARMENT ACCESSORIES FOUND IN THE IBIDA SITE, ROMANIA

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Abstract

Our paper presents the composition and the morphological characteristics of the surface and interior of certain garment accessories found during the archaeological diggings made at Ibida, in Slava Rusă, Tulcea county, Romania. Based on that, we evaluated a series of archaeometric attributes concerning their evolution from disposal to discovery. Our study involved the EDX and micro-FTIR techniques. By corroborating those analyses we could establish the composition of the base alloy and of the compounds that formed underground.

Keywords: *ancient metals; archaeology; archaeometry; EDX; micro-FTIR.*

Introduction

Researchers in the field of scientific conservation of cultural heritage items pay special attention to any discovery that, by its *contexts,* may complete the stratigraphic and chronological graph of human evolution, from an economic, social and cultural background perspective (cultural integration). In the case of an archaeological artifact, they are primarily concerned with the *discovery context*, but also with other aspects, such as: its conception and manufacture, its use, its disposal etc. The discovery context provides a series of important information for establishing the heritage elements and functions of the artifact. It focuses on *the mode of discovery* (by systematic archaeological digs, isolated finds during agricultural works, digs performed during construction works, landfalls caused by floods, isolated finds in old caverns, or in digs made by wild animals etc.), on *photographic and stratigraphic records* according to habitation layers (stratigraphic positioning), on determining the physical-chemical and micro-biological charge of the soil and on the *determination of the chemical composition* and certain archaeometric characteristics of the crust, or of the deposits and base alloy (morphology, texture, porosity, the microstratigraphic structure, the structural components of contamination etc.), on *evaluating certain transformations/processes/ structural, compositional effects,* to determine the evolution from disposal to discovery moment (pedological effects), or on establishing possible heritage elements and functions prior to disposal [1-8].

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Systematic studies of whole metallic artifacts, or on fragments thereof, from different historical periods, aim to determine the composition of alloys, to reveal the mechanisms involved in corrosion (chemical, electro-chemical and/or microbiological) and other processes that may have affected the artifact from its use period to its moment of disposal and during its underground stay, by identifying the compounds that formed during the three periods and even by establishing the possible influence of industrial pollution and of the fertilizers used in agriculture during recent periods. In that regard, researchers pay attention to three groups of structures that occur in the corrosion crust, especially in that of bronze artifacts, such as: *primary compounds* - formed during the artifact manufacture and utilization period by redox chemical processes (oxides, sulphates etc.), some as continuous and uniform coatings that form a noble patina, *secondary compounds* - resulted during the final phase of utilization and right after disposal, formed by redox electro-chemical processes assisted by acid-base ones, ionic exchange and hydrolisis (when oxi-hydroxides or hydroxi-salts form, halogenates, carbonates, sulphates, phosphates etc.) and sometimes thermal reactions (calcinations, recrystalizations etc.) due to burning, anthropic or natural. The third group of compounds, *the tertiary, or contamination compounds*, formed in the archaeological site under the influence of *pedological, chemical and micro-biological processes* (segregation, diffusion, osmosys, monolithization, fossilization, mineralization, hydration/dehydration, structural reformation etc.). The three types of structures are present in artifacts found both in disturbed and in undisturbed sites [9-15].

Among the modern artifact analysis methods, the most frequently used are the ones that operate in co-assisted systems, such as: EDX and micro-FTIR. They are non-invasive, with the exception of cases when micro-samples are taken, or when very small areas are cleaned [16-20].

The EDX technique provides both micro-structural and compositional information about the secondary phases and the inclusions, about the components of the base alloy and of the corrosion crust. By establishing the composition of the alloy one gets information about the options and/or the technical competences of the ancient craftsmen that processed the alloys (physical properties, color etc.). Minor elements my prove relevant when evaluating similarities or differences between metals from various periods, thus obtaining a technological progress chart [21-22].

The micro-FTIR technique, based on individual or group vibrations, serves to identify the molecular components in the analyzed material. By combining the two methods, one may establish the composition of the alloy and the corrosion products that formed on the surface of the artifact [23-28].

That information may establish: the alloy processing technology (with the presence or absence of refinement operations) and the casting, or forging technique, then one may establish the time and area of origin for the ore (based on specific micro-alloy, or impurities markers).

Our paper presents the results of EDX and micro-FTIR analyses performed on several metallic garment accessories that were found in the Ibida archaeological site, in the Slava Rusă village, Tulcea county.

Experimental

The garment accessories we selected for analysis were found by specialists at the Eco-Museal Research Institute, Tulcea, the Institute of Archaeology, Iasi and the Institute of Antheopology, Bucharest, during archaeological digs performed at the Ibida site, in the Slava Rusă village. We studied six fibula fragments, a belt clasp, two appliques, a buckle and a set of ten buttons, which were found at Ibida.

The six fibula fragments are shown in figure 1, as follows:

- *Fibula fragment* - ***F1*** (Fig. 1a), found at Ibida in 2002, area G, S1, square 16, - 1.80m, inventory number 45842, fragmentarily preserved. It is part of a fibula with a spiraled body, 36.26 mm long, with a 12.92 mm wide and 27.05 long needle (the preserved part), weighing

2.04 g. The lateral parts of the body are missing due to corrosion and of the lower part only a spiral was preserved wrapped around the body. The item is frequently found during the *barbaricum* and it is characteristic to the 4th century B.C..

- *Fibula fragment* - ***F2*** (Fig. 1b), found in the same place, year, area and depth as F1, but in square 17, and it has no inventory number and is in good state of preservation. The fragment preserved one lateral end of the cross shape with onion ends (Zwiebelknopffiebel) fibula type. Its maximum diameter is 10.40 mm, its total length 22.82 mm and it weighs 5.13 g. The item is characteristic to the second half of the 4th century B.C..

- *Fibula fragment* - ***F3*** (Fig. 1c), discovered in the same place, year and area as the ones above, but 1.20 m underground. It has no inventory number, its state of preservation is good and is shaped like a metallic strap with a fixing nut, whose head is missing. The item is curved, apparently being part of an arched garment accessory. It is approximately 31.30 mm long, its maximum width, along the nut line, is 10.37 mm and it weighs 1.74 g.

- *Fibula fragment* - ***F4*** (Fig. 1d), found in the same place, year, area and depth as F3, it has no inventory number and is in good state of preservation. Initially, this fragment was considered to be part of the previous (F3) and that was confirmed by our analysis. It is 28.60 mm long and is shaped like a metallic strap, 4.80 mm wide, weighing 0.98 g and with decorations consisting of vertical and angled incision lines on its arched part. One of its ends broadens and is continued by another element from a more complex garment accessory. Chronologically, it may belong to the 4th-6th century B.C..

- *Fibula fragment* - ***F5*** (Fig. 1e), found in the same place, year, area and depth as F3, with inventory number 45453, in good state of preservation. This fragment is a metallic strap, 35 mm long, bent and widening at one end, where there is circular hole 3.70 mm in diameter, apparently from a fixing nut for another element, similar to F3. It weighs 1.65 g and, chronologically, it may belong to the 4th-6th century B.C..

- *Fibula fragment* - ***F6*** (Fig. 1f), discovered in the same place, year and area as the ones above, but -0.35 m underground and in square 10. Its inventory number is 45848 and it is in a poor state of preservation. It is a fragment consisting only of a loop from the fibula body and a small part of the bottom. The exaggerated arching of the loop apparently happened after its disposal. The item was found in the soil used as filling for the tomb, a fact indicating an origin prior to that of the items above. The measurements for the item are: 21.70 mm for the amplitude of the loop, 15.40 mm for its opening and a weight of 3.76 g.

Fig. 1. Fibula fragments found at Ibida in 2002:
a – F1; b – F2; c – F3; d – F4; e – F5; f – F6.

The next set of accessories consists of:

- *Clasp* - ***C1*** (Fig. 2a), found at Ibida in 2006, in the Necropolis, in sector S2, with inventory number 48293, in a very good state of conservation. It is formed of two small plates, with symmetrical decorations cut out of them. The diameters of the two plates are slightly different, the one with a linking ring is 25.14 mm and the one with the hook 24.10 mm. Both weigh 5.49 g. Apparently it was a Medieval item that was lost in a Roman-Byzantine necropolis. We should mention that in Ibida there also are some Medieval tombs.
- *Applique* - ***A1*** (Fig. 2b), found at Ibida in 2003, in the Necropolis, in tomb M 39, with inventory number 46263, in a fair state of preservation. It is shaped as a fish, with two connection appliques at its "tail" and two nuts, of which only one is still visible, there being a hole where the other had been. Its dimensions are 30.65 mm in length, 19.45 mm maximum width and it weighs 2.85 g. It was dated to the 3rd-4th century B.C..
- *Applique* - ***A2*** (Fig. 2c), found at Ibida in 2001, Court G, sector S1, square 5, depth - 2.30 m (above the early Roman layer), with inventory number 45904, in a poor state of conservation. It is shaped as a disk with a hole in the center. Its diameter is approximately 38 mm, the diameter of the hole is 5 mm and it weighs 0.97 g. The exterior has simple decorations made of concentric circles, of which only two are visible near its center. It was dated to the 2nd-3rd century B.C..
- *Buckle* - ***B1*** (Fig. 2d), found at Ibida in 2001, in the Necropolis, in the Tudorca Crypt, with inventory number 45909, in a fair state of preservation. It has a rectangular loop with rounded corners and it preserved a needle that reaches over its rim. The item is 29.87 mm long and 19.77 mm wide and the needle is 22.72 mm long. It weighs 8.61 g. The item is specific to men clothing worn in the Danubian region during the 4th-5th century B.C.

Fig. 2. Garment accessories found during archaeological digs at Ibida:
a – C1; b – A1; c – A2; d – B1.

The third set of accessories consists of 10 spherical buttons with connection brackets, made of the same metallic material, of which we only studies one, labeled – **B2** (Fig. 3). They were found at Ibida, in 2006, the Necropolis, in tomb M 109, sector S2, squares 1-2, 1.02 m underground and the were inventoried under no. 48301 - 48310. They were found on the chest area of the person in tomb M 109. Their diameter is approximately 6.70 mm and they have a hole in their upper part. They also have a securing bracket 4.45 mm in diameter. They each weigh approximately 2.05 g, which may indicate that they have a hollow core. Apparently they constituted part of the clothing of a person buried in Ibida.

Fig. 2. Buttons **B2** found in 2006 at Ibida

The objects were analyzed by EDX and micro-FTIR techniques without sampling

a. The EDX Analysis

In the research was involved a scanning electron microscope, SEM VEGA II LSH model, produced by TESCAN, coupled with an EDX QUANTAX QX2 detector, manufactured by Bruker/ROENTEC Germany.

The Quantax QX2 is an EDX detector uses for qualitative and quantitative micro-analysis. The EDX detector is the third generation, the X-flash, that does not require liquid nitrogen cooling and is about 10 times faster than conventional Si (Li) detectors.

The technique, with micro-photogram view, imaging plays mapping (layout) investigated the surface atoms, and X-ray spectrum based on elemental composition determination (gravimetric or molar percentage of a microstructure or a selected area and assessment of composition variation ordered along a vector in the area or section analyzed.

b. The micro-FTIR Analysis

The spectra were recorded with a FT-IR spectrophotometer coupled with a microscope HYPERION 1000, both equipment from Bruker Optic, Germany.

The FT-IR spectrometer TENSOR 27, which is an advanced flexible desktop instrument suitable for routine applications as well as for laboratory research. The TENSOR 27 is designed for measurement mainly in the mid-infrared region. The standard detector is a DLaTGS with covers a spectral range from 4000 to 600 cm-1 and working at room temperature. The resolution is normally 4 cm-1 but it can go up to more than 1 cm-1.

Analyses were performed in the Laboratory of Scientific Investigation and Conservation of Culturale Heritage in the Platform of Interdisciplinary Training and Research, „Al.I. Cuza" University of Iaşi.

Results and Discussions

The surface and transversal section analyses revealed chemical and physical-structural characteristics of the items, which were then used to evaluate archaeometric attributes in regard to ore origin, alloy processing technology and object manufacture procedure. The results of our experiments identified the main compounds formed during the underground stay period from object disposal to its discovery.

By EDX analysis we identified the elemental composition in mass percentages of the residual patina - after the objects were cleaned (Tables 1 and 2) - and that of the base alloy (Table 3) of the 11 objects in our study.

Table 1. Chemical composition of the surface structures, in basic components

Samples	Elemental composition – weight percent (%)						
	Cu	Sn	Pb	Zn	Fe	Ag	Au
F1	26.361	1.993	-	-	0.401	-	-
F2	25.352	0.488	1.749	3.787	0.182	-	-
F3	20.611	3.346	4.512		0.501	-	-
F4	26.632	4.474	4.523		0.491	-	-
F5	63.602	0.756	3.384	9.353	0.315	-	-
F6	-	-	-	-	17.768	-	-
C1	2.401	-	-	-	-	94.313	3.236
A1	1.580	-	-	-	-	92.123	3.883
A2	25.556	0.958	2.041	4.230	0.265	-	-
B1	-	-	-	-	53.006	-	-
B2	-	2.868	23.652	-	-	-	-

Table 2. Chemical composition of the surface structures, in contamination elements

Samples	Elemental composition – weight percent (%)								
	Si	Al	Na	K	Ca	O	Cl	S	C
F1	0.447	0.454	-	-	-	48.814	0.172	-	21.358
F2	0.054	-	-	-	-	46.040	-	-	22.348
F3	0.128	0.3133	-	-	-	48.640	-	-	21.949
F4	0.145	0.276	-	-	-	43.963	0.142	-	19.353
F5	0.066	0.139	-	-	-	9.214	-	-	13.171
F6	3.314	3.035	8.157	0.663	1.399	53.558	0.421	-	11.685
C1	-	-	-	-	-	-	0.050	-	-
A1	-	-	-	-	-	-	0.016	2.398	-
A2	0.056	-	-	-	-	45.319	-	-	21.575
B1	1.832	0.777	6.452	-	2.764	29.621	0.364	-	5.185
B2	0.105	-	-	-	-	34.072	-	-	39.303

Based on their composition, we established that the item were made of four metals: bronze, silver, iron and lead. Apart from the basic element and the alloy components, we also identified traces of other components.

Surface structure analysis revealed the following:

- the base components in the F3 and F4 fibula fragments are Cu and Sn, their composition also containing Pb and Fe, which certainly came with the ore, an aspect emphasized by fragment F1, that did not contain Pb. All three had Al, Si, C and O in their surface structures and the F1 and F4 fragments also contained Cl.
- the F2 and F5 fibula fragments had a more complex composition, as their base alloy contained Cu, Sn, Pb, Zn, and Fe, and Cl was absent from their contamination elements;
- the base composition of the F6 fibula fragment had Fe and C, and as contamination elements there was Na, K, Ca, Al, Si, O and Cl;
- the C1 clasp and the A1 applique had Ag, Au and Cu in their surface structure composition and as contamination elements we found Cl and S in the A1 applique, and only Cl in the C1 clasp;
- the A2 applique had a base alloy composition of Cu, Sn, Pb, Zn, and Si, C and O, as contamination elements;
- the B1 buckle had Fe as main component of its surface structure and Al, Si, Ca, Na, Cl, C, and O as contamination elements;
- the buttons had Pb and Sn base components and Si, C and O as contamination elements.

Table 3 contains the chemical composition of the metallic core, which differs from that of the surface structures, because it contained none of the contamination elements. The bronze accessories (F1, F2, F3, F4, F5 and A2) contained C and O in their internal structure, which demonstrates that some of them were made by micro-alloying ore and that a weak refinement was applied, which should be excluded from the composition of the surface structures, before evaluating certain authenticity attributes. Similarly, for the iron based accessories (F6 and B1), the C and O elements in their internal structures had to be subtracted from their surface structure. A series of significant differences between the two types of structures were caused by the segregation processes of active metals (Zn, Fe etc.) toward the surface, where they formed corrosion products during the underground period [9-12]. In bronze items, those effects are strongly influenced by the distribution of tin in the volume phase of the object. Due to its amphoteric character and its tendency to agglomerate into micro-lens, tin may partially control both segregation and corrosion processes. Moreover, on the surface of bronze objects the Sn(IV), Pb(II) and Zn(II) cations tend to form hydrogel coatings that have the Liessegang effect [17-19]. Unfortunately, the objects were aggressively cleaned on site before being brought for analysis, which compromised the archaeological context.

Table 3. The chemical composition of the metallic core.

Samples	Elemental composition – weight percent (%)								
	Cu	Sn	Zn	Fe	Ag	Au	Pb	C	O
F1	90.724	4.190	-	0.712	-	-	-	1.586	2.788
F2	64.223	0.337	10.135	0.221	-	-	0.631	8.535	15.918
F3	86.021	7.497	-	0.498	-	-	2.279	2.634	1.072
F4	80.927	7.848	-	0.553	-	-	3.150	2.152	5.371
F5	78.743	0.625	12.934	0.409	-	-	3.979	0.722	2.587
F6	-	-	-	62.608	-	-	-	1.260	36.132
C1	4.191	-	-	-	92.309	3.500	-	-	-
A1	3.137	-	-	-	93.630	3.232	-	-	-
A2	78.254	1.336	13.429	0.604	-	-	2.190	2.070	2.117
B1	-	-	-	98.310	-	-	-	0.373	1.317
B2	-	4.480	-	-	-	-	55.589	5.864	34.067

Based on the specific group vibrations, the micro-FTIR analysis determined the nature of the corrosion products in the surface structures.

By comparing the spectral data with reference spectra and relevant publications [27, 28] we identified the main components formed on the surface of the items, those forming the residual patina that remained after the cleaning procedures.

Table 4 lists the main spectral columns, with representative peaks, and their corresponding ions for every object under analysis.

Table 4. The spectral readings of the ions identified in the objects under analysis.

Ion type	Spectral readings (cm^{-1})	The analyzed object
Carbonate	670-745; 800-890; 1040-1100; 1320-1530	F1, F2, F3, F4, F5, F6, A2, B1, B2
Sulphide	570-680; 960-1030	A1
Chloride	610-630; 900-1050	F1, F4, F6, C1, A1, B1
Stanate	600-700	F1, F2, F3, F4, F5, A2, B2
Silicate	860 – 1175	F1, F2, F3, F4, F5, F6, C1, A1, A2, B1, B2
alluminate	800 – 920	F1, F3, F4, F5, F6, B1
Aquo- and hydro-compounds, coordination water	2550-3500	F1, F2, F3, F4, F5, F6, A2
physically bound waters	3500-4000	F1, F2, F3, F4, F5, F6, A2

The spectral readings indicated that apart from the C1 clasp and the A1 applique, all the other artifacts contained the carbonate, silicate and allumino-silicate groups. The F1, F4, F6, C1, A1 and B1 items featured the presence of the chloride anion and the A1 applique contained sulphide.

By combining the EDX and the micro-FTIR data we may conclude that the F1, F3 and F4 fibula fragments were objects cast in bronze made of ores based on Cu, Sn, Pb and Fe, which were subsequently struck and refined. The F1 item did not contain Pb, indicating that a different ore than that of F3 and F4 was used for it. Also, the F2 and F5 fibula, together with the A2 applique, were also cast and refined in bronze made of ores based on Cu, Sn, Pb, Zn and Fe, and for this alloy they also used ores that contained Zn, the safest choice of polysulphide ores. The presence of C and O in the internal structures of bronze items demonstrates that in the alloy manufacture process, refinement was weak or completely absent.

The F6 fibula and the B1 buckle are of cast and forged iron, the base alloy being made from pirite ores. The C1 clasp and the A1 applique were made of gold based ores, by pyro-metallurgy, using silver lumps and also polysulphide ores. After casting into small, open molds, the item was struck and refined.

The 10 buttons were made of alloys based on Pb and Sn ores, which were then cast.

All the garment accessories under study contained Cl in their surface structures, from the archaeological site, which triggered the alteration processes.

During their underground period the bronze items suffered serious segregation processes of their active metals (Zn and Fe), that altered by dissolution under the influence of phreatic and rain water. Most of the alteration effects of the surface structures were based on cumulative and competitive processes of the redox, acid-base and complexation type, under the influence of factors in the archaeological site. Those processes were completed by monolithization, which included several contamination elements from the soil. The corrosion crusts of the bronze medical instruments contained chemical compounds such as: oxides (CuO, Cu_2O, Fe_2O_3, Fe_3O_4, SiO_2 etc.), base carbonates ($CuCO_3 \cdot Cu(OH)_2$, $CuSO_4 \cdot 3Cu(OH)_6$ etc.), hidroxo-clorides ($Cu_2(OH)_3Cl$, $CuCl_2 \cdot 3Cu(OH)_2$ etc.).

The silver items had Cl in their surface structures and one (A1) also contained sulfur, from its manufacture and use period, originating in organic compounds from human skin, with which it came in contact.

Most of the compounds in all the items under study, formed shortly after object disposal. In the case of bronze items, those compounds evolved in time according to the activity of the coating agents in the hydrogels of Sn(IV), Pb(II) and Zn(II) cations, which provided a relative protection during the underground period of the objects.

The corrosion crusts of the iron objects mainly featured inert corrosion products, by the Fe_3O_4 magnetite, together with carbonates, chlorides and other oxides [29-30].

Conclusions

By combining the EDX and the micro-FTIR data we may conclude that the F1, F3 and F4 fibula fragments, of which the F1 item does not contain Pb, were objects cast in bronze made of ores based on Cu, Sn, Pb and Fe, which were subsequently struck and refined. Also, the F2 and F5 fibula, together with the A2 applique, were also cast and refined in bronze made of ores based on Cu, Sn, Pb, Zn and Fe, and for this alloy they also used ores that contained Zn. The presence of C and O in the internal structures of bronze items demonstrates that in the alloy manufacture process, refinement was weak or completely absent. The F6 fibula and the B1 buckle are of cast and forged iron, and the A1 appique and C1 clasp were made of ores based on Ag gold lumps, cast and forged. The 10 buttons were made of alloys based on Pb and Sn ores, which were then cast.

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During their underground period the bronze items suffered serious segregation processes of their active metals (Zn and Fe), that altered by dissolution under the influence of phreatic and rain water and also of contamination elements from the soil. The corrosion crusts of the bronze contained chemical compounds such as: oxides (CuO, Cu_2O, Fe_2O_3, Fe_3O_4, SiO_2 etc.), base carbonates ($CuCO_3 \cdot Cu(OH)_2$, $CuSO_4 \cdot 3Cu(OH)_6$ etc.), hidroxo-clorides ($Cu_2(OH)_3Cl$, $CuCl_2 \cdot 3Cu(OH)_2$ etc.).

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