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THE IDENTIFIED EFFECTS OF DEGRADATION IN ARCHAEOLOGICAL ARTIFACTS WITH OVERLAPPED METALS USED IN AUTHENTICATION

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Abstract

This paper presents the experiment results obtained by applying non-invasive methods (OM, SEM-EDX, XRF) on metallic artifacts from the 2nd and the 3rd centuries A. D. (discovered in the Văleni-Boteşti and Gabăra-Moldoveni sites, Neamţ County), with components from different overlapped metals (copper/iron), to determine the surface and the internal microstructure (cross-section), corrosion products distribution and the effect of the two metals in the alteration processes. The results revealed some attributes used in authentication, the determination of the conservation state and allowed us to establish proper procedures for the active conservation and the restoration of those artifacts.

***Keywords**: archaeological artifacts, overlapped metals, OM, SEM-EDX, XRF*

Introduction

Archaeological materials are an important source of primary information which complete the chronological image of human evolution from the point of view of economic development and that of social life, as well as cultural connections with previous civilizations. If we consider the archaeological material in regard to the degradations undergone in the given conditions, to the conservation state and the alteration mechanisms of metals in the soil, respectively, starting from physical aspects (fragments, cracks, holes, etc.) to chemical ones, from the formation of corrosion crusts to the bulks with or without metallic cores, we can draw some conclusions concerning the archaeo-metallurgical aspects, the ancient technologies, the methods used to obtain the objects or the origin of the metals used therein.

The processes of physical deterioration and chemical alteration of the artifacts made up of homogeneous alloys mainly composed of alloy as Cu-Sn, Cu-Zn, in the case of bronzes or brasses and as Fe-C. in the case of cast irons or steels, are of special interests both for archaeologists and for the restoration or conservation specialists. The metallic objects, especially interesting and important from a scientific view point, are also metallic items with different compositions which interacted in the environment they lied in. Generally speaking, such pieces were discovered in the cremation or inhumation tombs [1 – 4].

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In the dig-site environment processes of chemical, electrochemical or microbiological corrosion [5 – 10] occur as a result of the interaction of the soil with the metallic items. The altered metallic alloy has on its external surface a *crust* which may be thin, smooth and with a homogeneous structure, or thick, coarse and with a mostly heterogeneous structure. Significant similarities/differences appear even within the objects with the same structure, from the same historical period, with the same utility or which were obtained using the same technology. The analyses with the SEM-EDX optical and electronic microscopy and with X-rays techniques (X-rays photography, X-rays diffraction, X-rays fluorescence, etc.) carried out on the crusts of the metallic artifacts from various historical periods revealed major differences from a structural and compositional point of view. They were generated by internal or external factors as well as by the conditions of the objects were found in [10 – 11]. Thus, the modern investigations applied on metallic objects from various historical periods allowed us to determine the modifications undergone in the environment where items were found; especially interesting are the results concerning the interactions which took place between the artifacts made of homogeneous alloys but which, accidentally or not, were in contact with metals with a different structure, or with artifacts made of two different, overlapped metals.

In the archaeological practice they found objects belonging to both situations, namely, iron knife blades with bronze rivets [12] or iron knife blades adorned with small brass plates (Figs. 1 and 2), as well as clothing accessories of the spring fibula type (Fig. 3) consisting of an iron pin on which copper alloys coils were wound up.

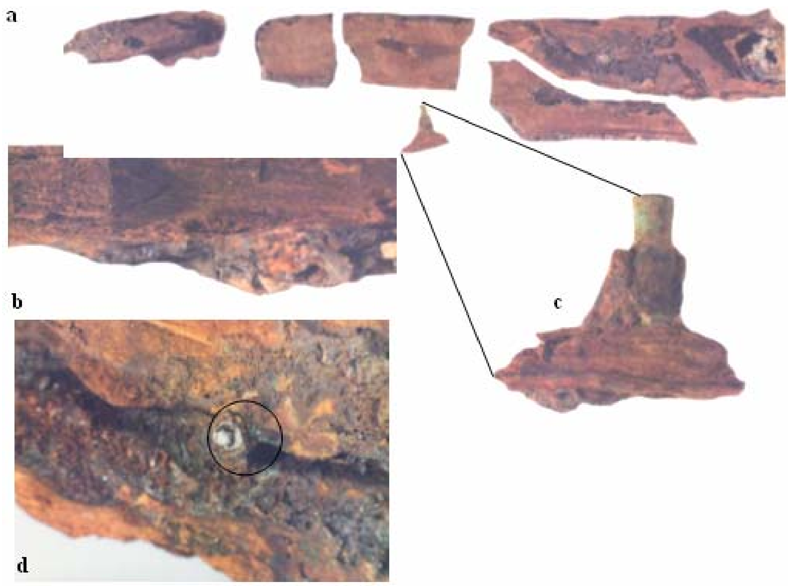

Fig. 1. Fragments of iron knife with bronze rivets.

Fig. 2. Iron knife decorated with small brass plate.

Fig. 3. Spring fragment with iron pin.

This paper presents some of the results obtained by studying the influence of the pedological factors on the surface and on the internal structures of the fibula-type artifacts with springs made of various overlapped alloys, which were found in two important and complex archaeological sites, namely, the Dacian-Carpian necropolis in Gabăra – Moldoveni [1-3] and the necropolis in Văleni, the Boteşti commune, both in the Neamț County [4].

Experiment data

Description of the Artifacts

The clothing accessories discovered in the cremation and inhumation tombs, or in the different layers of the archaeological site, were analyzed with non-invasive techniques (optical and electronic microscopy, X-rays fluorescence, X-rays diffraction) from a structural and a compositional point of view. In that respect, we analyzed the internal and external structures of the metallic alloys and determined the corrosion products and the elementary compositions of the processed alloys. Thus, from the Văleni – Boteşti necropolis, Neamț County, we will mention the case of some objects used for decorative purposes, especially fibulae belonging to two different systems: the first one was influenced by the human factor before being abandoned by the cremation point, the second one was affected by natural processes undergone in the surrounding environment.

1. In 1964 in the Văleni – Boteşti necropolis, Neamț County, they found a fragment made of an iron alloy on which copper alloy coils were wound up (Fig. 4), with inventory number 11687

Fig. 4. Spring fragment, inventory number 11687.

Most of the coils got lost in the surrounding environment while those still distinguishable were completely mineralized.

2. The fibula with the inventory number 7628 was discovered in an inhumation tomb (M 419) 0.80 m. underground. The fibula was in a fragmentary state, its body being intact but the spring was broken in two pieces (Fig. 5).


a b

Fig. 5. Fibula, inventory number 7628: a- image of the piece; b – spring detail (cross section).

Experiment Techniques

Optical Microscopy.

The microscopical investigations were carried out using an Olympus SZ60 stereomicroscope at various magnifying degrees, up to the maximum of 60X.

The SEM-EDX Electron-scan Microscopy

The investigations were carried out using a SEM VEGA II LSH scanning electronic microscope manufactured by the TESCAN Co., in the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by BRUKER / ROENTEC Co., Germany

The X-rays Fluorescence. The X-rays fluorescence analyses were carried out with a portable INNOV-X SYSTEM device, with a tungsten anti-cathode tube, 35 KV, 40 μA, 30 seconds exposure time; data processing was done with specialized software.

The X-rays diffraction was performed with a Bruker D8 diffractometer by using the samples taken from the corrosion crusts of the artefacts.

Results and Discussions

Fragment with the inventory number 11687. On the whole, the processes of chemical alteration and physical degradation of the two alloys produced different surface effects. Thus, the surface analyses of the iron alloy at various magnifying settings of the stereomicroscope revealed a discontinuous corrosion crust with deposits made of primary, secondary and tertiary chemical compounds of iron, predominant being the goethite with cracks and the vesicle-type formations, either single or as clusters (Figs. 6 – 9).

The surface effects generated by the processes of chemical alteration of the copper alloy are evident in the discontinuous corrosion crust formed on the mineralized bulk. Thus, the chemical compound deposits are non-uniformly distributed in the external corrosion layer, but, microscopically we also found some cracks, micro-craters and holes (Figs. 10 – 12).

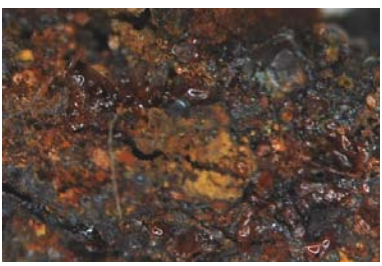

Fig. 6. Cracks and secondary chemical compounds in the external layer of the corrosion crust, 60X.

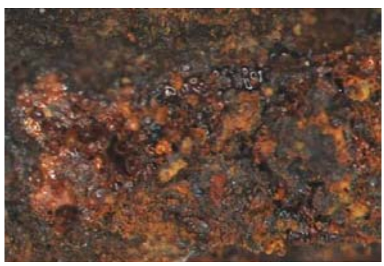

Fig. 7. Secondary and tertiary chemical compounds in the corrosion crust, 60X.

Fig. 8. Single vesicant-type formations, 60X.

Fig 9. Vesicant-type formations, 60X.

The contamination of the corrosion crust of the copper alloy was revealed by means of the analyses with the X-rays fluorescence spectometer. The determined elements were 78. 42 ± 0.61% Cu, 8. 68 ± 0.22% Fe, 2.03 ± 0. 11% Zn, 9. 23 ± 0.30% Sn, 1.64 ± 0.14% Pb.

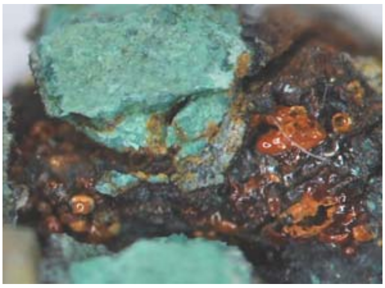

Fig. 10. Corrosion crust with cracks, 40X.

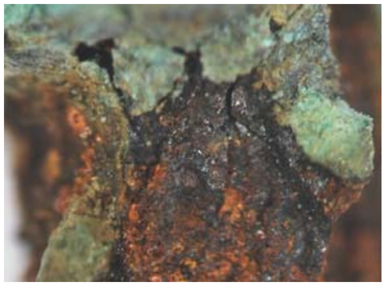

Fig. 11. Exfoliated foils from the corrosion crust, 40X.

Fig. 12. Loss of the mineralized alloy by corrosion processes, 40X.

The analyses with the SEM-EDX scan microscopy revealed the structures of the two alloys and the microstructures which got embedded in the archaeological site. Thus, the corrosion crust formed on the mineralized bulk of the iron pin is a discontinuous one, with cracks and craters (Fig. 13).

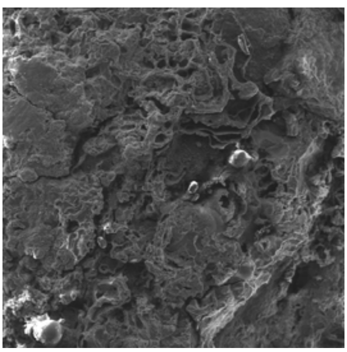

Fig. 13. Corrosion crust on the spring pin, inventory number 11687, 200X.

In the elementary composition we identified Fe, C, Cu, Al, Si, Cl and O, according to the EDX spectrum shown in Fig. 14 and in Table 1. The presence of Cu in the external layer of the corrosion crust formed on the iron alloy indicates its contamination by the copper alloy.

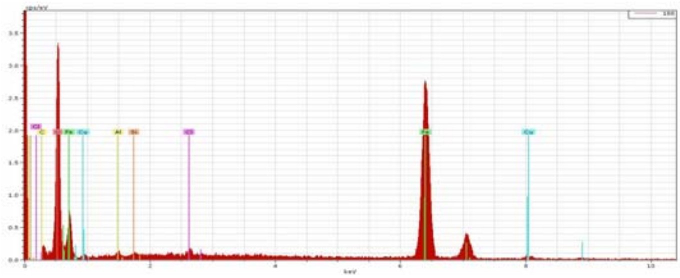

Fig. 14. The EDX spectrum obtained for the fibula pin, inventory number 11687.

Table 1. Elementary composition determined on the spring pin, inventory number 11687

Element	Weight %	Atomic %	Error in %
Carbon	2.130569	5.347884	0.649839
Iron	63.49231	34.27574	1.81471
Copper	2.090957	0.992024	0.146225
Chlorine	0.557484	0.474077	0.060374
Aluminium	0.589078	0.658221	0.079779
Silicon	0.525222	0.563802	0.069314
Oxygen	30.61438	57.68825	4.26663

In the corrosion crust of the iron alloy we identified complete and broken vesicles (Figs. 15 and 16) with compositions in which we identified elements as Fe, Cl and O, according to the EDX spectrum shown in Fig. 17 and Table 2.

Fig. 15. Vesicant-type formations, 500X.

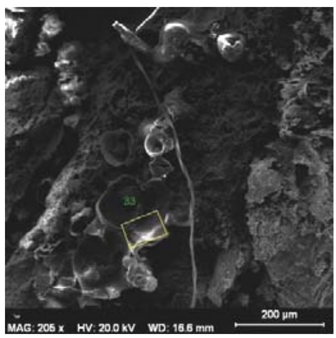

Fig. 16. Vesicant-type formations, 205X.

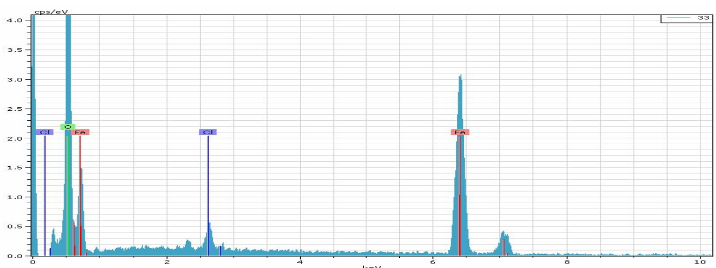

Fig. 17. The EDX spectrum obtained for the vesicant-type formations from Fig. 16.

Table 2. Elementary composition determined on the vesicles from Fig. 16

Element	Weight %	Atomic %	Error in %
Iron	52.7678	24.77945	1.605875
Chlorine	2.446141	1.809483	0.151281
Oxygen	44.78605	73.41107	6.573497

The corrosion crust of the copper alloy is composed of a non-uniform external layer with cracks, craters and microstructures which got embedded from the archaeological site (Figs. 18 – 20).

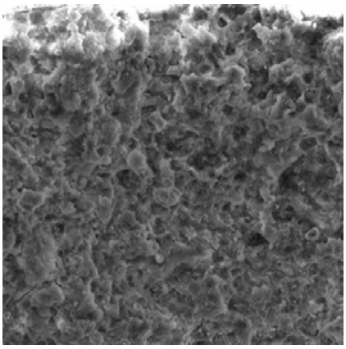

Fig 18. Discontinuous corrosion crust formed on the mineralized bulk, 800X.

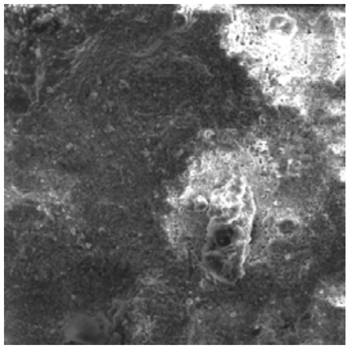

Fig. 19. Microstructures embedded in the corrosion crust, 1150X.

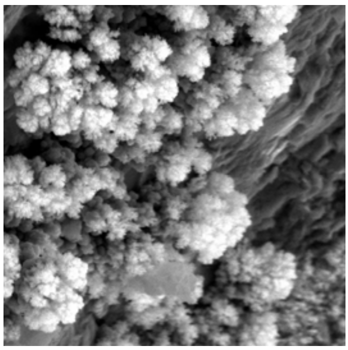

Fig. 20. Contaminated corrosion crust, 3650X.

In the composition of the external layer we identified elements from the composition of the copper alloy and elements which got embedded from the archaeological site, according to the EDX spectra in Figs. 21 and 22 as well as in Tables 3 and 4.

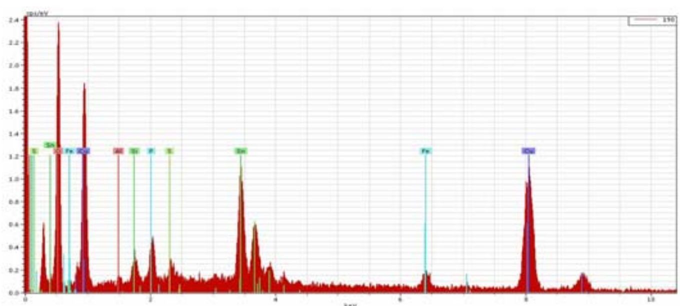

Fig. 21. The EDX spectrum obtained in the corrosion crust from Fig. 18.

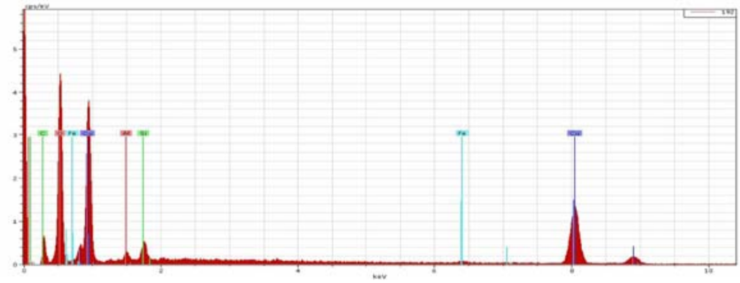

Fig. 22. The EDX spectrum obtained in the corrosion crust from Fig. 19.

Table 3. Composition determined on the corrosion crust from Fig. 18

Element	Weight %	Atomic %	Error in %
Silicon	1.128199	1.271145	0.096653
Copper	40.74876	20.29166	1.181918
Iron	2.635163	1.493135	0.139745
Sulphur	0.884978	0.873332	0.075982
Tin	17.53279	4.67364	0.564923
Phosphorus	1.786421	1.825078	0.11789
Aluminium	0.264519	0.310229	0.055741
Oxygen	35.01917	69.26178	5.18837

Table 4. Composition determined on the corrosion crust from Fig. 19

Element	Weight %	Atomic %	Error in %
Silicon	2.12309	1.97684	0.13882
Copper	51.26519	21.09695	1.543411
Iron	0.6654	0.311579	0.064207
Aluminium	1.213644	1.176278	0.106643
Carbon	4.80701	9.32011	0.857533
Oxygen	40.45197	66.11824	5.521326

*Fibula 7268***.** The processes of chemical alteration and physical deterioration of the two metals (Fe from the pin alloy and Cu from the alloy of the body and that of the coils) contributed to the formation of some secondary crusts with corrosion products of copper on the body, as well as secondary compounds which belong both to the copper and to the iron on the spring.

On the fibula body we identified a continuous secondary crust without elements characteristic to the physical deterioration, layered as follows:

- an external layer with deposits of secondary compounds (copper chlorides and cuprous sulphides) with their specific colors, namely, green and green-bluish, respectively (Figs. 23 and 24);
- an intermediary layer made of cupric oxides;
- metallic core.

Fig. 23. External corrosion layer on the fibula body.

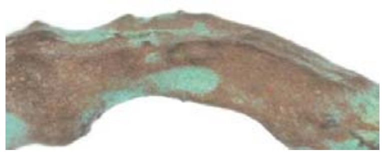

Fig. 24. Secondary compound deposits on the fibula body.

In the spring cross-section we identified a corrosion crust formed on the copper alloys coils and on the mineralized iron pin (Fig. 25).

Stratigraphically, the secondary corrosion crust consists of:

a light green discontinuous external layer with surface effects in which the cracks and the holes are predominant (Fig. 26);

an intermediary layer;

the bulk with the partially mineralized core.

In the external corrosion layer of the spring we identified copper chlorides and cuprous sulphides, as well as secondary compounds of iron, especially goethite. The iron corrosion products are located mainly between the spring coils.

The iron pin on which the coils were wound up has the form of a tube empty on the inside (Fig. 27).

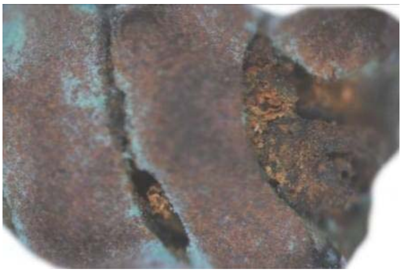

Fig. 25. Copper alloys coils wound up on the iron pin, 40X.

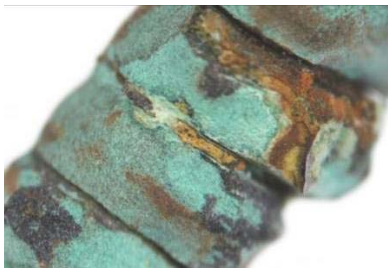

Fig. 26. External layer of the corrosion crust formed on coils, 40X.

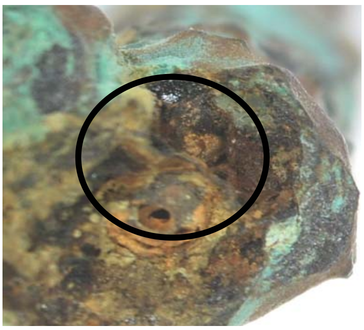

Fig. 27. Iron pin in the form of a tube empty on the inside, 40X.

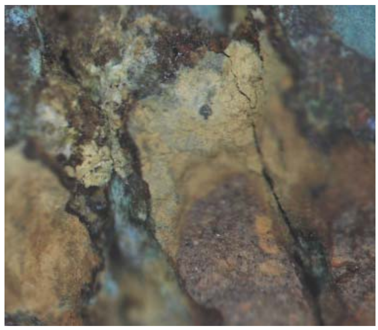

Fig. 28. Contamination of the crust with components from the soil, 40X.

In the corrosion crusts from the body and the spring of the fibula the chemical compounds have a non-uniform distribution; the elements embedded by contact or the ones from the archaelogical site (Fig. 28) were revealed with an X-rays fluorescence spectometer. Thus, based on the XRF spectra, we identified thr elements Cu, Fe, Zn, Pb, as in Table 5.

Table 5. Elementary compositions identified on the components of the fibula with the inventory number 7628

Elements	On the body %	On the spring %
Cu	93.36 ± 0.55	91.32 ± 0.51
Fe	0.46 ± 0.05	2.22 ± 0.08
Zn	5.80 ± 0.14	6.00 ± 0.13
Pb	0.38 ± 0.07	0.47 ± 0.07

The corrosion compounds resulted from the alteration of copper were determined with a Bruker D8 diffractometer, used on samples taken from external layers. The obtained results confirm the existence of a secondary corrosion crust on the spring with primary and secondary chemical compounds from the class of copper chlorides and cuprous sulphides, according to the XRD diffraction spectrum shown in Fig. 31.

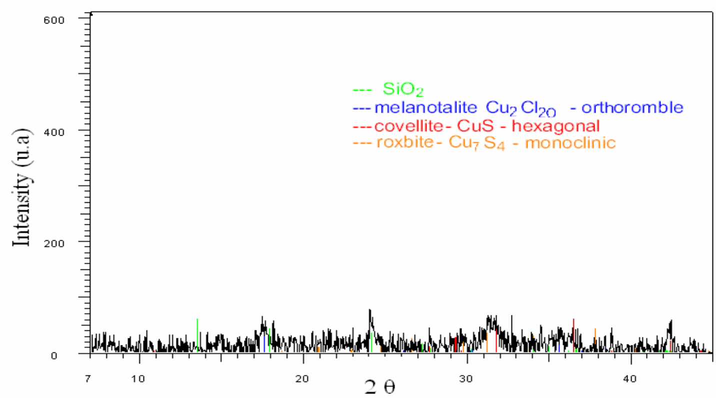

Fig. 29. The XRD diffraction spectrum obtained for the fibula with the inventory number 7628.

Springs with copper alloy coils wound up on an iron pin were also found in the necropolis of Gabăra, the Moldoveni commune, Neamț County. The first fibula fragment (Figs. 30 a and b) with the **inventory number 423** has a part of the spring covered with bone fragments embedded in the crust as a result of contact interactions. The second fragment with the **inventory number 12836** (Fig. 31) was well preserved, with a continuous and relatively homogeneous corrosion crust.

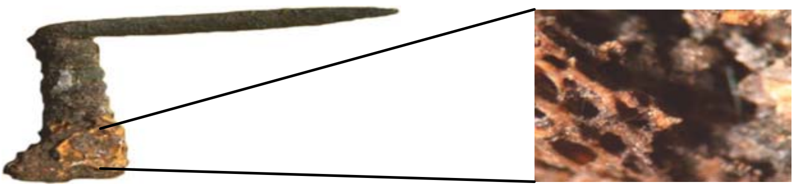

Fig. 30. Needle and spring of the fibula with the inventory number 423
a – general aspect; b. bone detail, 40X.

Fig. 31. Spring fragment, inventory number 12836.

The surface analyses of the fibula with the inventory number 423 determined the morphology of the primary corrosion crust formed on the surface of the processed alloy. This crust is continuous, homogeneous and with uniformly distributed corrosion products on the fibula needle (Fig. 32).

Fig. 32. External layer of the corrosion crust.

Fig. 33. Spring iron pin on the needle, inventory number 423.

The corrosion crust on the spring is non-homogeneous with corrosion products of copper and iron. In the cross-section of the pin on which the copper alloy coils were wound up, the iron corrosion products are concentrated (Fig. 33).

The second fragment of the spring discovered at Gabăra – Moldoveni had a continuous and relatively homogeneous primary corrosion crust, but with non-uniformly distributed corrosion products (Fig. 34). That crust got contaminated with soil elements from the surrounding environment(Fig. 35).

Fig. 34. Corrosion crust on the spring, inventory number 12836.

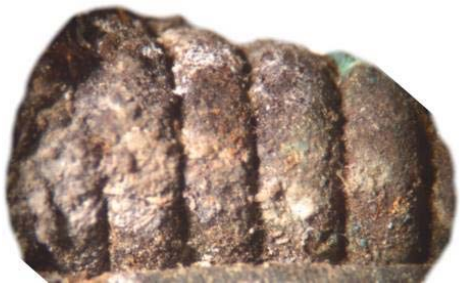

Fig. 35. Contaminated corrosion crust, inventory number 12836.

The analyses with the X-rays fluorescence spectrometer revealed the elementary compositions of the two fibula fragments. Thus, on the spring and the needle of the fibula with the inventory number 423 we identified the elements Cu, Fe, Zn, Sn, Pb, according to the XRF spectra in Figs. 36 and 37 as well as in Table 6.

Table 6. Elementary composition determined on the fibula with the inventory number 423

Elements	Spring, %	Needle, %
Cu	59.76 ± 0.41	87.04 ± 0.62
Fe	25.24 ± 0.26	0.60 ± 0.06
Zn	8.27 ± 0.15	4.55 ± 0.15
Sn	1.61 ± 0.10	2.97 ± 0.21
Pb	5.11 ± 0.17	4.83 ± 0.26

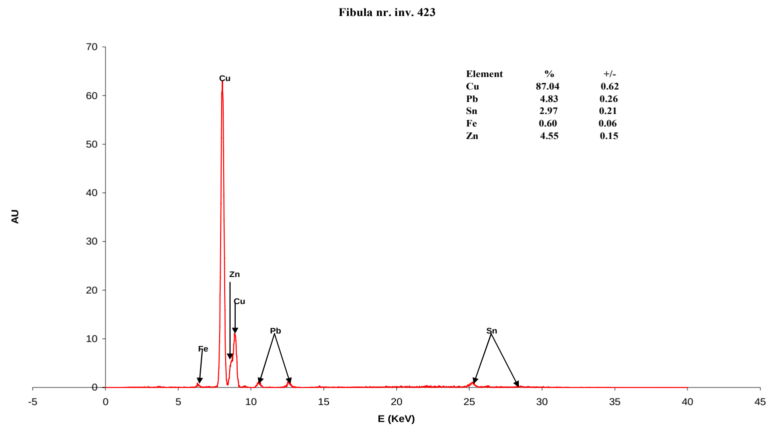

Fig. 36. The XRF spectrum obtained for the fibula needle, inventory number 423.

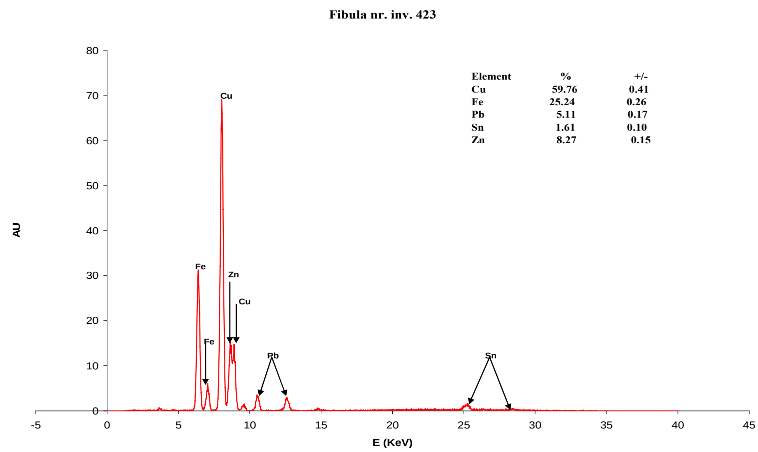

Fig. 37. The XRF spectrum obtained for the fibula spring, inventory number 423.

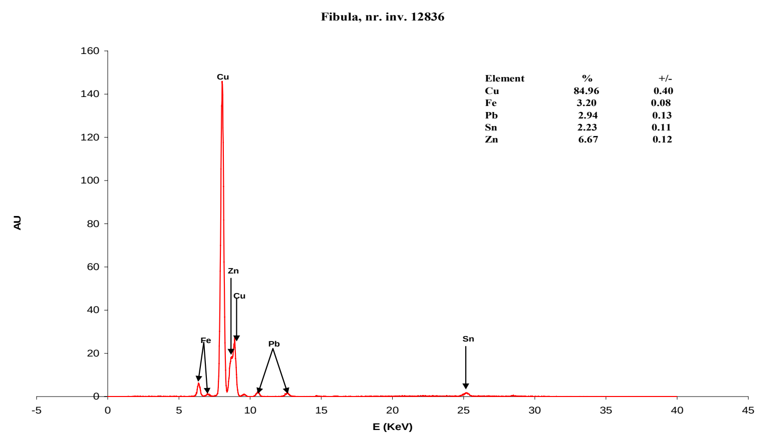

Fig. 38. The XRF spectrum obtained on the fibula spring, inventory number 12836.

The elements identified in the corrosion crust of the spring with the inventory number 12836 belong to the copper alloy, as a result of its contamination by the iron corrosion compounds, according to the XRF spectrum in Fig. 38 and in Table 7.

Table 7. Elementary composition determined for the fibula with the inventory number 12836

Elements	Spring 12836/1, %
Cu	84.96 ± 0.40
Fe	3.20 ± 0.08
Zn	6.67 ± 0.12
Sn	2.23 ± 0.11
Pb	2.94 ± 0.13

Conclusions

Scientifically, as regards the deterioration and alteration of metals found in soil, a special attention is given to the fibulae whose springs were made by overlapping two different metals, i.e. copper alloy coils were wound up on an iron pin. There are complex chemical processes that occurred in the surrounding environment and, as a result of interactions, corrosion crusts formed with holes and irregular concretions of primary and secondary compounds. The chemical processes in the springs area also extended to the fibula coils and, in some cases the corrosion products were also found in the crusts formed on their bodies.

Some parts of the springs of the fibula-type metallic artifacts from the 2nd and 3rd centuries A.D. were made using two technological processes for metal manufacturing: one for the iron alloys, the other for the copper alloys. The obtained metal items were made manually, in the case of the springs, by winding up the copper alloy coils on an iron pin.

The cross-sections of the springs revealed that for the iron pin they used *hollow tubes*, some of which were found in an partially or completely mineralized form, others got lost in the surrounding environment as a result of the alteration processes.

The pieces cremated before being abandoned had a modified internal structure but, after having been abandoned and during the period they lay buried, the two metals, namely, Fe and Cu evolved differently, interacting with elements from the surrounding area and also with each other. On the whole, the heating process changed the inner structure of iron and, in some cases thin films, similar to glazing, formed. There were also formations of various types (dew drops, profiled relief or vesicles) which rendered specific properties to the iron alloy, making it immune to the alteration factors and processes.

In contrast to the modifications in the iron, the copper alloys had a fast evolution after being burned. The crushing and the erosion was often encountered in the physical deterioration process, unlike the processes which occurred in the pieces extracted from the soil profile. An explanation for the chemical alteration and physical deterioration of the copper alloys could involve the presence of some elements such as tin or zinc in the composition of the alloy. Those elements have low melting points and produce structural reformation. The melting temperature of tin is 231.9ºC while zinc is brittle at temperatures higher than 200ºC and easily turns into powder, a fact which explains the nature of the secondary corrosion crusts and the effects produced by the chemical alteration and physical deterioration on the cremated artifacts made of copper or copper alloys.

The electrochemical corrosion processes in the artifacts discovered in the inhumation tombs or in the soil contributed to iron corrosion easier than in the case of copper. From the archaeological sites they extracted fragments of fibulae springs on which there were only deposits of corrosion products resulted from the alteration, brittling and erosion of the iron metallic pin.

The identification of the effects of degradation in artifacts made of overlapped metallic structures allows us to establish certain characteristics used as attributes in the authentication.

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