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A TYPICAL SURFACE FORMATIONS FOUND ON THE CORROSION LAYER OF IRON ARTEFACTS

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ABSTRACT

The paper presents the experimental results obtained by applying non-invasive methods (OM, SEM-EDX, XRF) on two iron artefacts from the IInd and the IIIrd centuries A.D. (discovered in the incineration graves from Gabăra-Moldoveni and Văleni-Boteşti, Neamt County), for determining the surface and the internal microstructures (cross-section), corrosion products distribution and some atypical formations resulted from the incineration processes. The results allow the rendering evident of some attributes used in authentication, the determination of the conservation state and the establishing of the proper procedures for the active conservation and the restoration of the artefacts.

KEYWORDS: iron archaeological artefacts, atypical formations, OM, SEM-EDX, XRF

1. Introduction

The study of the cultural inheritance by involving some methods and techniques from the interdisciplinary fields such as history, physics, chemistry, geochemistry, mineralogy, biology, pedology, etc., develops more and more a new field, namely, the *scientific conservation*. The "conservation state" is the result of the complex actions which have led to the chemical and physical alterations of the metallic artefacts. In the case of the archaelogical artefacts one must emphasize the difference between the conservation state acquired in the lying environment, also called *natural conservation*, and the state created as a result of the laboratory interventions, called *artificial conservation or active preservation*.

The need for a "science" of the artefacts restoration appeared at the same time with the first materials digged out from the archaelogical sites. The restoration is defined as the "science" which deals with the restoration of the works of art [1, 2]. C. Randi considers in "The Theory of Restoration" that *"the restoration constitutes the methodological moment of acknowledging any work of art in its physical consistency and in its double aesthetical and historical polarity with a view to transmit it to the future"* [3]. In the field of the archaelogical metals, the concept of restoration implies the bringing of the objects to a form as close as possible to the original one by preserving the time patina. In the laboratory work the application of some mechanical and chemical treatments should be done, wherever possible, to preserve the corrosion crusts even if these do not contain impressions or microstructures from the archaelogical site, thus maintaining the time patina. In the case of the pieces subjected to some burning processes before being abandoned, or when they include physical remains or various impressions from the archaelogical site, the laboratory workings aim to their maintaining by artificial preservation; in the case of the completely mineralized fragments whose form is difficult to state, the revaluation is carried out by scientific researches, by drafting some new treatments for the stabilization, consolidation and artificial preservation.

The categories of objects discovered in funeral urns are especially important and their revaluation is being done in the stage when they are rendering evident the palaeo-technology and the socio-religious traces, such as in the case of adornments, vestimentary accessories or even some iron fragments. In this context, the objects discovered in the cremation places, in funeral urns or graves, constitute a peculiar category of cultural assets from the view point both of the physico-chemical alterations in the lying grounds and of the interventions accomplished in laboratories. In what the physico-structural and chemical alterations on the iron metallic artefacts are concerned, there have been identified structures which give specific properties to alloys under various forms, namely, smooth glassy-shaped, vesicle-type, spherical or oval, empty on the inside, dew drops-shaped or with relief profile [4 – 6], the last two being encountered only in the cremated pieces.

This paper presents the atypical structures of the relief profile-type formations resulted after the cremation of some iron alloys objects discovered in two archaelogical sites from the Neamţ County, namely, the Dacian necropolis from Văleni, Boteşti commune, and, respectively, the Dacian-Carpian necropolis from Gabăra-Moldoveni [7 – 10].

2. Experimental Part

2.1. Description of the Artefacts

a. In the Văleni – Boteşti necropolis there have been found out fragments of an iron necklace (Fig. 1), with the inventory number 7308, in a cremation grave (M 2) in a lidded urn together with ash-cleaned calcined bones as well as glass and amber beads [7].

b. The fragments of an iron necklace (Fig. 2), with the inventory number 11761, have been discovered in Văleni – Boteşti in a cremation grave (M 306) in a lidded urn together with ash-cleaned calcined bones and beads fragments [7].

Fig. 1. *Necklace fragments, inventory number 7308*
a – general image; b – fragment detail

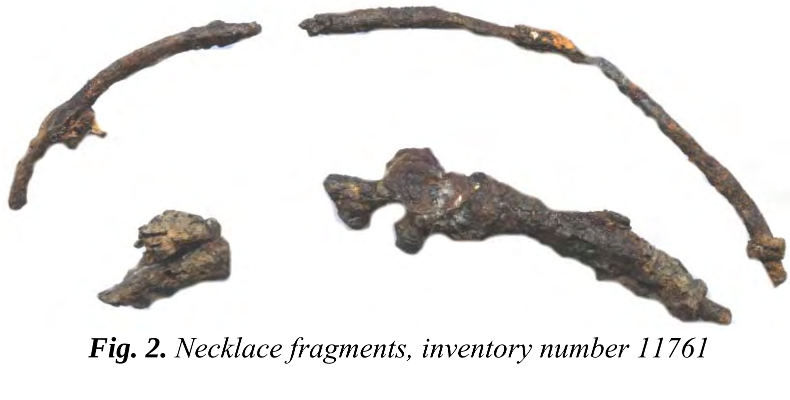


Fig. 2. *Necklace fragments, inventory number 11761*

2.2. Optical Microscopy

The microscopical researches have been carried out on an Olympus SZ60 stereomicroscope at various magnifying powers up to the maximum 60X.

2.3. The SEM-EDX Electron-scan Microscopy

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

2.4. The X-rays Fluorescence

The X-rays fluorescence analyses have been carried out with a portable INNOV-X SYSTEM apparatus, with a tungsten anti-cathode tube, 35 KV, 40 µA, 30 seconds exposure time; the data processing has been done with a specialized software.

The corrosion of the iron takes place in the presence of water and oxygen.

A simple way for the formation of the rust, Fe_2O_3, implies the following reactions:

$Fe_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$

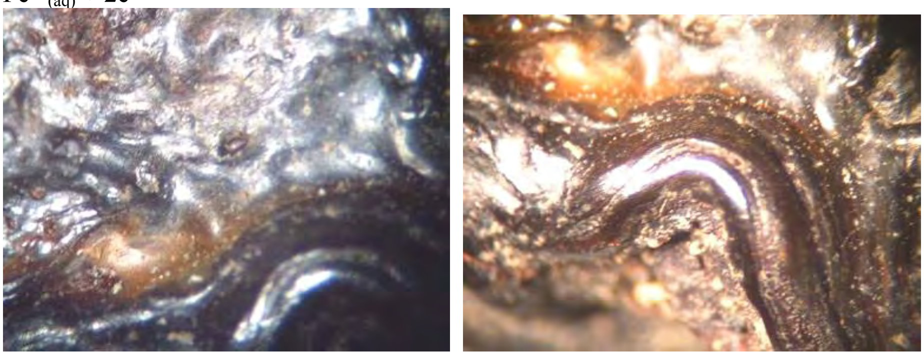
$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \rightarrow Fe(OH)_{2(s)}$

$Fe(OH)_{2(s)} + ½O_{2(g)} \rightarrow Fe_2O_{3(s)}$

The corrosion of the iron pieces is taking place faster than in the case of the bronze ones, the compounds resulted after the alteration being the goethite, $Fe_2O_3·H_2O$, the lepidocrocite, $Fe_2O_3·H_2O$, the magnetite, Fe_3O_4, etc. The forming order of the primary, secondary or tertiary compounds is the following: the hematite, α-Fe_2O_3, the goethite, α-FeO(OH), the lepidocrocite, γ-FeO(OH) and the (inert) magnetite, Fe_3O_4. [11, 12].

The pieces extracted from the cremation graves are characterized by the presence in the corrosion crusts of some small formations under the form of dew drops or irregular formations with relief profile. The most corrosion crusts whose formations have relief profile have been identified at the adornment objects, iron basket-type pendants, bracelets fragments and vestimentary accessories extracted from the cremation graves.

These formations have smooth glassy surface without deposits with corrosion products (Figs. 3 a and b). In the areas with this type of formations, the alloy has specific properties, making it inert under stable microclimate conditions.



a b

Fig. 3. *Corrosion crust with relief formations on an artefact found in a cremation grave at Văleni-Boteşti, Neamţ*

Preservation States

The necklace fragments with the inventory number 7308 have a brittle metallic core, and in the corrosion crusts there have been identified formations with relief profile (Figs. 4 a – c) and mineralized textile fibers (Figs. 5 a – c).

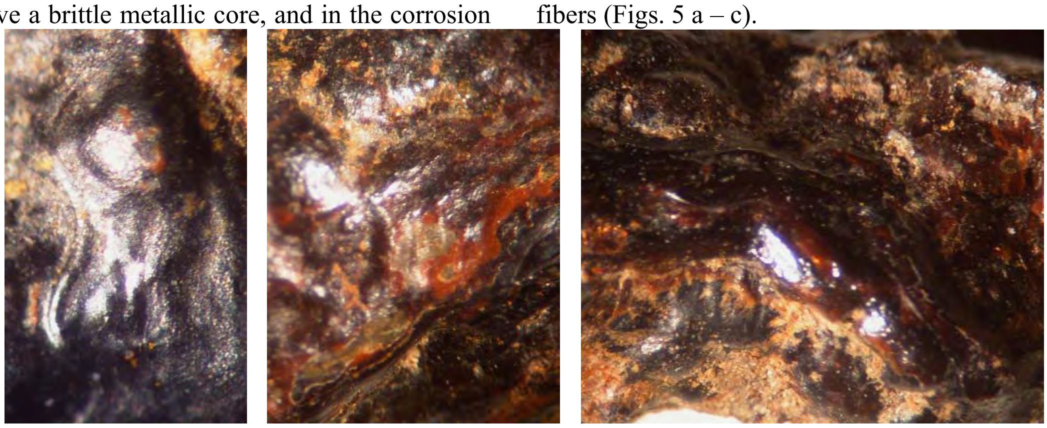


Fig. 4. *Formations with relief profile resulted on the artefact with the inventory number 7308*

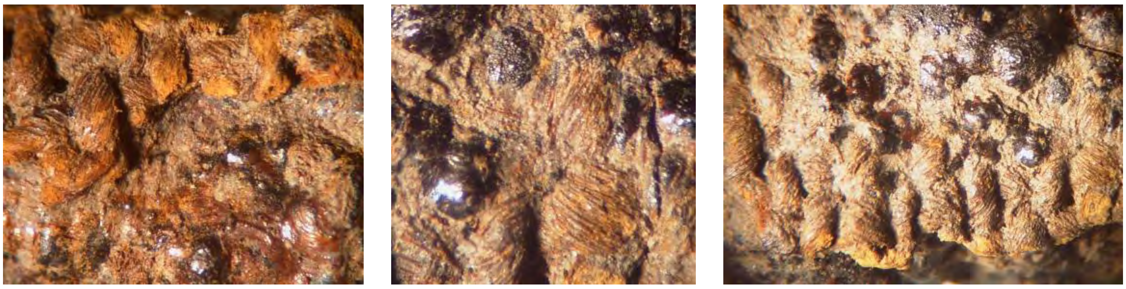


***Fig. 5.** Impressions of mineralized textile fibers, inventory number 7308*

In the case of the necklace fragments there have been identified formations with relief profile (Figs. 6 a – a), entire and broken vesicles (Figs. 7 a and b) as well as a bone fragment (Fig. 8).

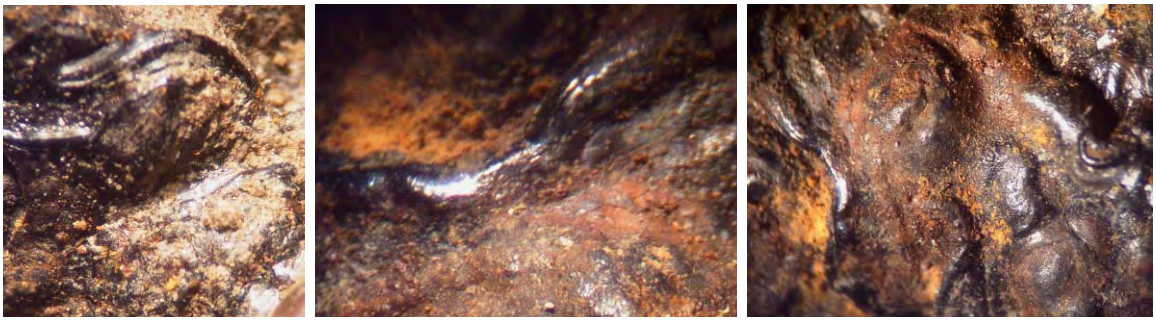


***Fig. 6.** Formations with relief profile resulted on the artefact with the inventory number 11761*

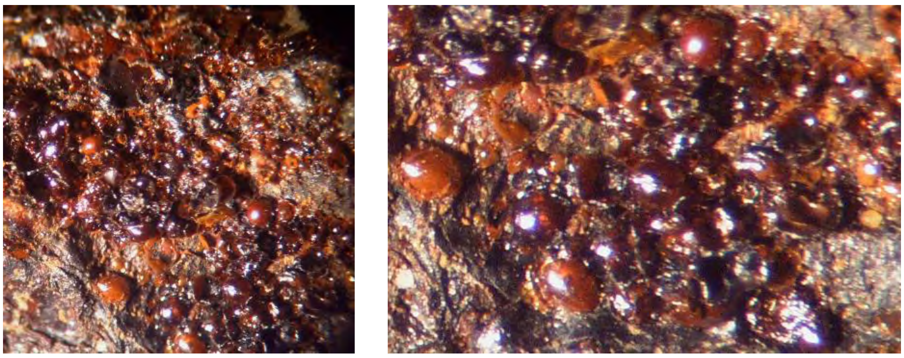


***Fig. 7.** Vesicant-type formations*

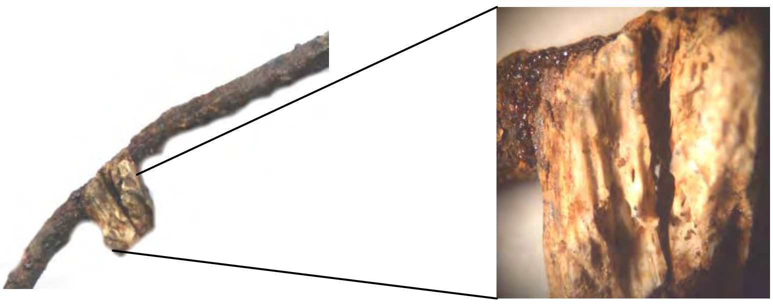


***Fig. 8.** Bone fragment on the artefact with the inventory number 11761*

The formations with the relief profile as well as the dew drops ones are the result of the burning processes. The formations have usually smooth glazing surfaces without deposits of primary, secondary and tertiary compounds of iron, and, when not deteriorated, they constitute a protection barrier for the metallic alloy. Under the action of the deterioration process, the formations with the relief profile are destroyed, thus resulting cracks or holes (Figs. 9 a and b).

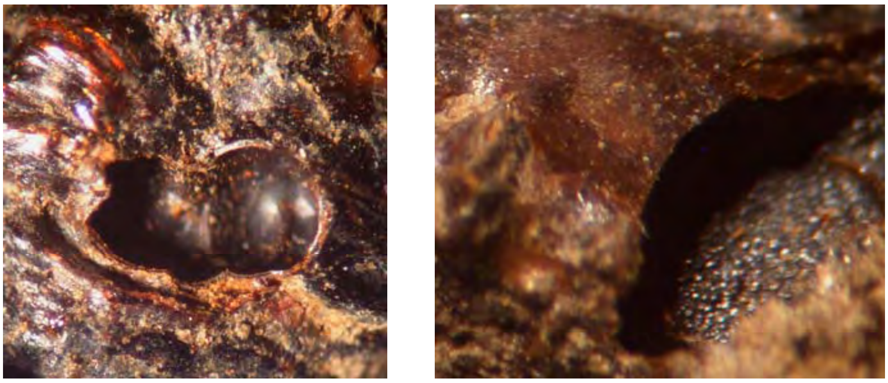


Fig. 9. *Corrosion crust with deteriorated formations, inventory number 7308*

The corrosion crusts, the embedded microstructures from the archaelogical site as well as the distribution of the elements in the external layers have been analysed with the electronic microscope. Thus, for the artefact with the inventory number 7308 we have noted formations with the relief profile with micro-cracks (Fig. 10) in whose composition there have been determined the elements Fe, Si, Al, Ca, P according to the EDX spectrum (Fig. 11) and to the Table 1.

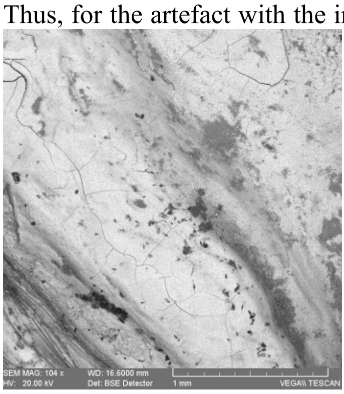


Fig. 10. *Image of the surface on the formations with relief profile, 100 X*

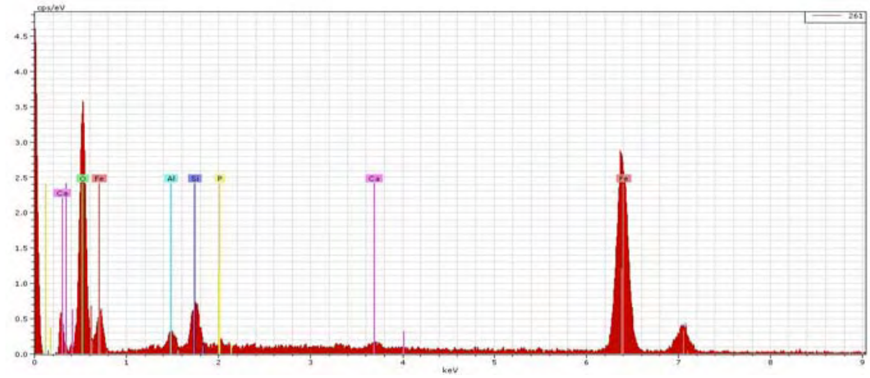


Fig. 11. *EDX spectrum obtained for the formation from Fig. 10*

Table 1. *Elementary composition determined on the basis of the EDX spectrum from Fig. 11*

Element	Weight,	Atomic	Error
	[%]		
Iron	58,69289	30,86762	1,627004
Silicon	4,713831	4,929573	0,253801
Aluminium	1,980366	2,155739	0,149242
Calcium	0,69423	0,508762	0,060853
Phosphorus	0,820202	0,777757	0,076827
Oxygen	33,09848	60,76055	4,44303
	100	100	

In the case of the artefact with the inventory number 11761 the analyses carried out on the SEM-EDX electronic microscope have rendered evident formations with relief profile and, respectively, relatively uniform surfaces but contaminated with microstructures from the archaelogical site (Figs. 12 and 13). From a composition view point, in these formations there have been determined the elements Fe, C, Si, Al, Ca, K, Mg, P according to the EDX spectrum (Fig. 14) and to the Table 2.

Fig. 12. *Image of the surface on the formations with relief profile, 100 X*

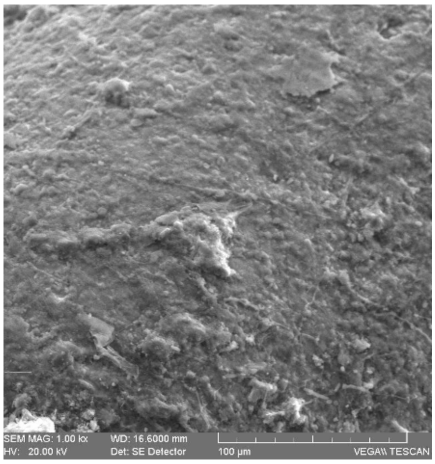


Fig. 13. *Image of the contaminated surface, 1000 X*

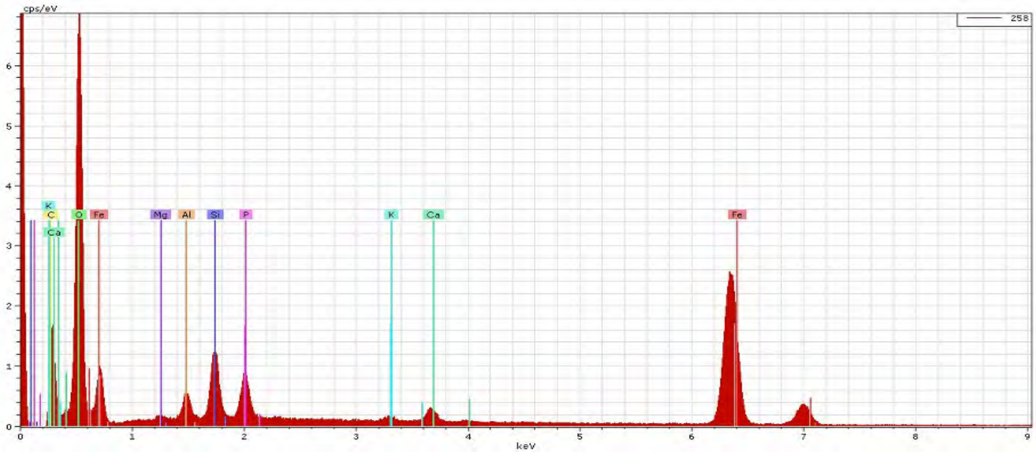


Fig. 14. *EDX spectrum obtained for surface from Fig. 13*

Table 2. *Elementary composition determined on the basis of the EDX spectrum from Fig. 14*

Element	Weight	Atomic	Error
	[%]		
Iron	43,4956	19,00375	1,289623
Silicon	4,012562	3,48605	0,216992
Phosphorus	2,808675	2,212593	0,149444
Carbon	4,485019	9,111272	0,993904
Aluminium	1,763928	1,595174	0,124248
Calcium	0,96972	0,590384	0,062337
Potassium	0,488672	0,304968	0,047076
Magnesium	0,614659	0,617067	0,070545
Oxygen	41,36117	63,07874	5,227605
	100	100	

The analyses carried out on the bone sample from the artefact with the inventory number 11761 have rendered evident a complex casuistics, namely, formations of the entire and broken types vesicles (Fig. 15), the bone embedded in the corrosion crust (Fig. 16) and, respectively, formations with relief profile (Fig. 17) in whose composition there have been determined the elements Fe, Si, Al, Ca, P according to the EDX spectrum (Fig. 18) and to the Table 3.

The vesicant-type formations have been generated both during the cremation period by the vitrification – glazing processes, and, subsequently, by metabolic processes under the influence of the *Ferrobacillus* bacterium which oxidates Fe^{2+} into Fe^{3+} in the presence of the chloride anion or of the *Thiobacillus ferrooxidans* one which oxidates Fe^{2+} and S^{2-} [5].

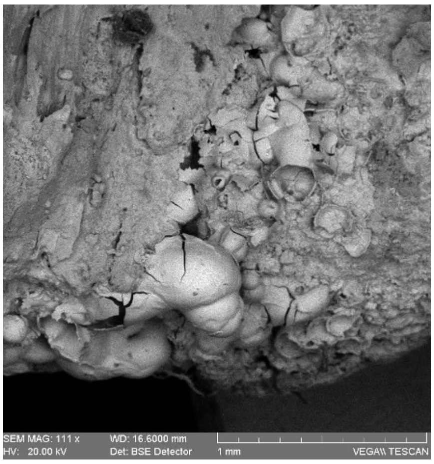


Fig. 15. *Vesicant-type formations, 110 X*

Fig. 16. *Bone image, 150X*

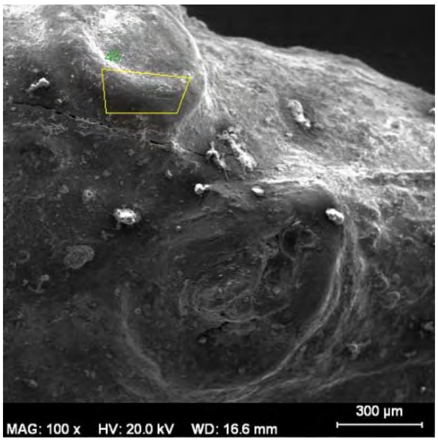


Fig. 17. *Image with formations with relief profile, 100 X*

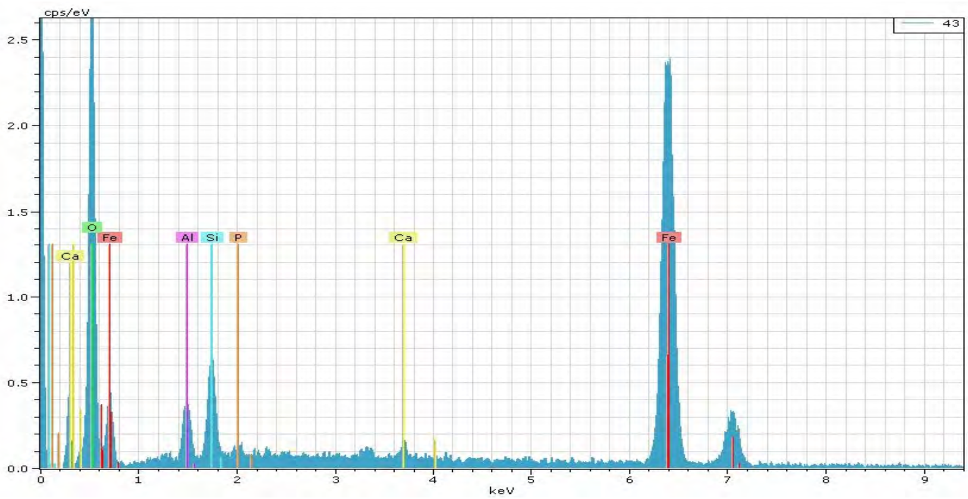


Fig. 18. *EDX spectrum obtained on one of the formations with relief profile from Fig. 15.*

Table 3. *Elementary composition determined on the basis of the EDX spectrum from Fig. 16*

Element	**Weight**	**Atomic**	**Error**
	[%]		
Iron	62,41941	34,52579	1,770829
Silicon	4,442616	4,886303	0,258556
Aluminium	2,571272	2,943778	0,192766
Calcium	0,577411	0,445044	0,063097
Phosphorus	0,752013	0,74999	0,083259
Oxygen	29,23728	56,4491	4,326339
	100	100	

Formations with relief profile have also been identified at the artefacts discovered in the archaelogical diggings at Gabăra - Moldoveni, Neamţ County. Thus, in the Dacian-Carpian necropolis there has been found out a small bell without clapper and without a part of the base circumference (Fig. 19). This piece has been analysed, from a structural and composition view point, by non-invasive analytical techniques by means of an X-rays fluorescence spectrometer and an Olympus SZ60 stereomicroscope, respectively. Thus, there have been rendered evident the formations with relief profile (Fig. 20) and the elementary composition of the artefact. On the external part the corrosion crust is discontinuous with formations whose profile are of the relief type but without elements of physical deterioration (holes, cracks or craters). In the fastening area of the clapper the corrosion crust has been contaminated as a result of the contact with some other artefacts from the site as well as with elements from the soil according to the X-rays fluorescence spectrum (Fig. 21). In the contaminated area the elementary composition is 41.20% Fe, 44.52% Cu, 1.04% Sn, 13.24% Pb.

Fig. 19. *Small bell*

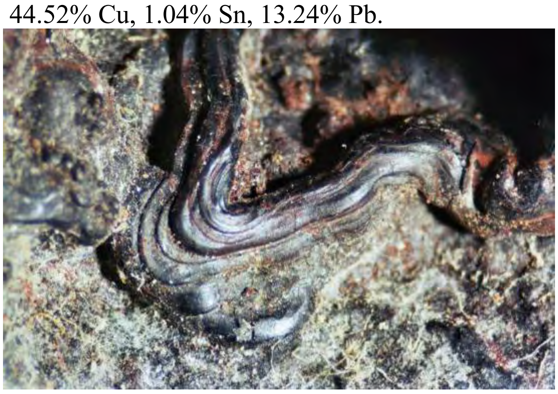


Fig. 20. *Corrosion crust with relief profile formations*

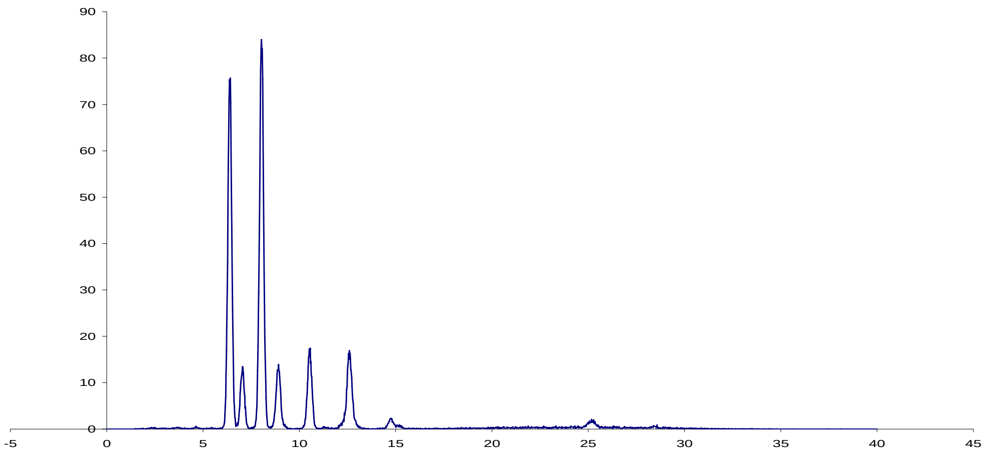


Fig. 21. *The XRF spectrum obtained for the small bell.*

4. Conclusion

The obtained experimental results have led to the following conclusions:

- in the corrosion crusts of the studied cremated pieces there have been identified the following formations: the smooth, glassy and glazing types; the dew drops types; the entire or broken types vesicles; the relief profile type;
- the chemical and physico-structural analyses have rendered evident the presence of the corrosion crusts of different nature from the view point of the alloy origin and of the compound type;
- the small vesicles type formations have been generated by vitrification – glazing processes and, subsequently, by metabolic processes under the influence of the Ferrobacillus bacterium which oxidates Fe^{2+} into Fe^{3+}, in the presence of the chloride anion or Tiobacillus Ferrooxidans one which oxidates Fe^{2+} and S^{2-};
- the formations with relief profile have no defined form but are characterized by the continuity of the external layer.

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