Study of Some Atypical Degradation Processes of an Iron Archeological Piece

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The paper presents the experimental results concerning the study of the chemical nature and the structure of the archaeological bulk of a fibula which is an atypic case, very seldom encountered at the iron pieces from the 2-nd and 3-rd centuries A.D.; bone impressions have also been conserved on these fibula. The elements characteristic for the alteration phases of the metals during the lying period have a structural representation in the external corrosion layer by the non-uniform arrangement of the chemical components resulted from the base metal and from the archaeological site. These have been determined by direct and non-invasive methods such as the optical microscopy and the SEM-EDX.

Keywords: OM, SEM-EDX, corrosion, microstructural components, conservation state, iron archaeological piece

The tendency of metals to return to their primary state, i.e. that of ore, is known, but the stopping of the alteration processes after the discovery and excavation from the site by conservation and restoration operations is a complex activity which allows the rendering valuable and the treasuring of some ancient civilizations.

The phenomenon of the corrosion of the artefacts made up from copper or iron alloys, the nature, the composition or the mechanism of the formation of the structure of the natural patinas and of the corrosion crusts, the impact of the chemical pollution by industrialization or the usage of the fertilizers in agricultural works are only some of the subjects discussed with a view to the degradation and authentication of the metal objects which have been lying for a long time in soil, air or water [1 – 11].

Two major processes are generally involved in the degradation of a metallic artefact, namely, the corrosion by chemical, electrochemical and microbiological alteration processes, and the erosion by physico-mechanical processes. That is why during the scientific investigation of the metallic artefacts the researchers are paying attention to the identification of the structural differences of the bulks of some pieces having the same historical age discovered in the same archaeological site.

The mechanism by which there are produced the chemical alteration and the physical deterioration of the metals in soil, and, respectively, the formation of the primary and secondary compounds and of the evolutive cracks with the formation of networks or holes as well as of some segregation, diffusion, crystalline structural reforming processes cannot be generalized for all types of metallic artefacts. The nature of the chemical components and their arrangement in the archaeological bulk depend on two groups of factors, namely, the endogenous (internal) and the exogenous (external) ones [12 - 14]. The endogenous factors are connected with the nature of the material and the manufacturing technology. The exogenous factors include, besides the climatic factors (temperature, humidity, atmospheric pressure, air currents/ wind, rainfalls), the radiative factors, natural chemical agents, pollution and the pedological ones (dynamics and the aggresivity of the underground water, soil movements, landslides).

The mechanism of the degradation of the iron artefacts is very different from the bronze ones within the same manufacturing technologies (casting, forging, rolling) and of the type of the artefact. The chemical alteration of the metal archaeological pieces during the lying period is influenced by numerous parameters varying in time, a series connected by the internal factors (chemical composition and the manufacturing technology) as well as by the external ones induced by the microclimatic conditions and the physico-chemical characteristics of the soil (structure and texture of the soil, permeability to oxygen and the soil humidity, microbiological activity, presence of the organic materials and their decomposition). Other exogenous factors influence indirectly the chemical changes of the metals by the impression and, respectively, by the embedding/incrustation of microstructural elements adjacent to the piece (nummulitic structures, bone, textile fibres, glass, wood) etc.

Similarly, the mechanism of the process of physical deterioration depends on the type of the artefact which has a specific wear for the contact areas and a characteristic stress due to the exogenous factors.

In the case of the pieces discovered in the cremation urns the corrosion processes have been influenced, besides the above mentioned factors, by the anthropic factors, more exactly by the change of the metals structure before their abandonment time, by their passing through fire and the subsequent formation of some external layers under the form of glazing, layers which can be rendered evident by the optical microscopy and the scanning electron one.

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By involving both the optical microscopy and the Scanning Electron Microscopy this paper studies the nature and the microstructural arrangement of the chemical components resulted from the corrosion and contamination processes, characteristics very important in the authentication, the determination of the conservation state and the establishing of the proper procedures for the active conservation and the restoration of the artefacts.

Experimental part

Description of the Piece

The studied piece is an iron fibula (fig. 1) which has been discovered as a result of some archaeological diggings in a Dacian – Carpathian necropolis on the Gabăra Hill, Moldoveni, Neamţ county. The object is on a fragmentary state but the body is intact, with a large loop, the pin is broken into three pieces with the sharp end thrust into the case from the fibula body; only parts of the spring coils have been kept. A bone impression has been conserved on the spring. One should note that in the researched necropola the cremation graves have been scattered among the inhumation ones [15].

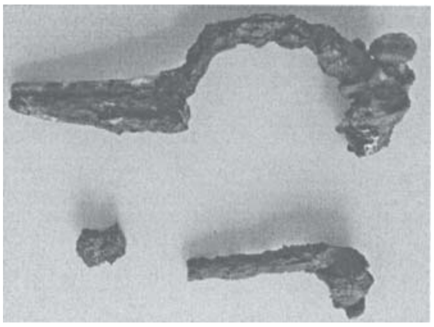


Fig. 1. Fibula, inventory number 13

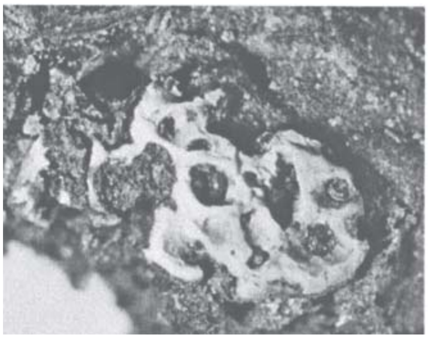


Fig. 2 Bone impressions

Conservation State of the Piece

From the conservation view point the piece shows the brittleness of the metallic core. The corrosion crust presents deposits with complex structures resulted from the pedological processes from the archaeological site, embedding as well the contamination microstructures (silica, caolin, etc.).

The experiments have been carried out directly on the sample by involving only non-invasive techniques without any sample taking.

Optical Microscopy.

The direct study of the corrosion layers with the help of the optical microscopy has the advantage of obtaining some immediate results without intervening upon the artefacts. Thus, the fine patina or the coarse crust do not tolerate changes in samples taking and preparing; the data comparing is done at the same parameters. The microscopic observations have been done with an Olympus SZ60 stereomicroscope.

SEM-EDX

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

The microscope, entirely computer operated, contains an electron gun with tungsten filament that may achieve a 3nm resolution at 30KV, with a magnifying power between 13 and 1,000,000 X in the “resolution” mode, a gun potential between 200 V and 30 kV, a scanning speed between 200 ns and 10 ms per pixel. The working pressure is lower than $1 \cdot 10^{-2}$ Pa. The obtained image can be constituted by the secondary electrons (SE) or by the backscattered ones (BSE), respectively.

Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis. Quantax QX2 is a 3-rd generation X-flash detector, which does not require liquid nitrogen cooling and is about 10 times faster than the traditional Si(Li) detectors.

Results and discussions

The studied object has been manufactured with an iron alloy. The piece has been discovered as a result of some archaeological researches between 1957 – 1959 and the microscopic observations carried out after about 50 years of museum microclimate have allowed the obtaining of some important information on the conservation state. Microscopically there has been identified a non-uniform layer determined both by the discontinuities created by the corrosion products, resulted from the chemical processes of the iron degradation (fig. 3, a – b) as well as by some formations which appear in the external layer on the body, pin and spring of the piece.

The iron degradation in time has been caused by some redox processes of chemical or electrochemical nature as well as by some acid-basic, complexing, hydrical and thermal processes. The formations from the body and the spring of the fibula have a smooth external layer, similar to a glazing, apparently uniform, of a brown-reddish colour (fig, 4, a – c), being the result of the thermal and hydrical processes.

The examination of these structures with the SEM-EDX has rendered evident a relatively uniform surface with micro-cracks networks (fig. 5, a – b) having the composition Fe, C, P, Si, Ca, Al, Na (fig. 6). The composition of one of the glazed formations is presented in table 1 on the basis of the SEM – EDX spectrum shown in figure 7.

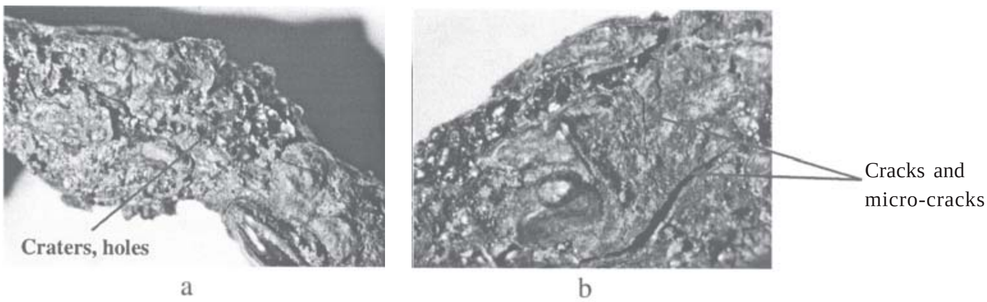
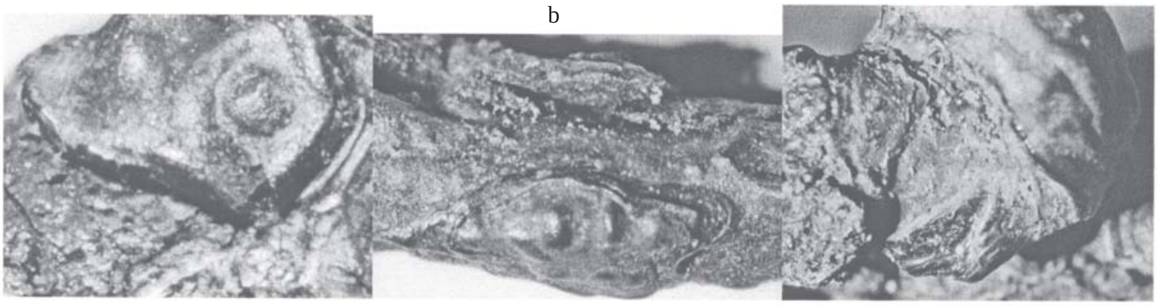


Fig. 3 a-b. Discontinuous external layer due to the corrosion deposits holes, craters and cracks on the fibula with the inventory number 13 b

a



c

Fig. 4 a-c. Discontinuous external layer due to some glazer-type formations
Formations on the fibula with the inventory number 13

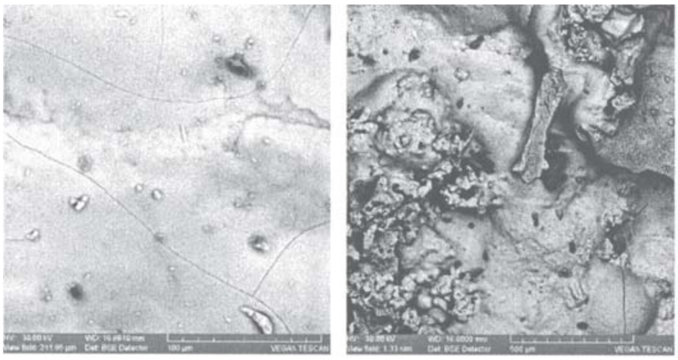


Fig. 5 a,b. SEM images on the fibula with the inventory number 13

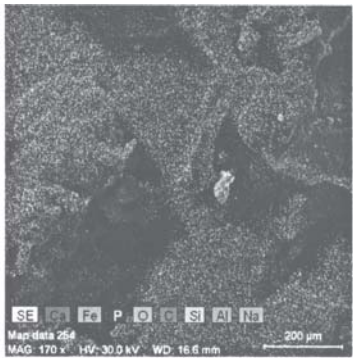


Fig. 6. Element Mapping on external part (glazer)

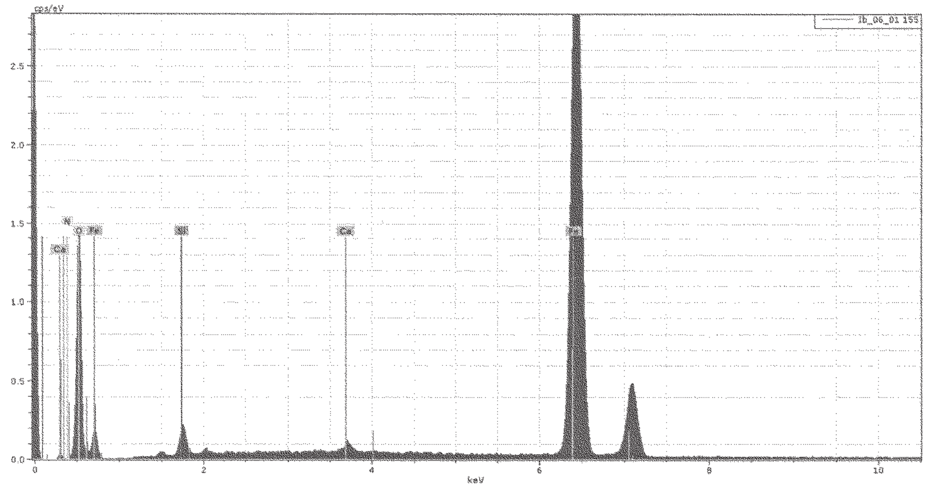
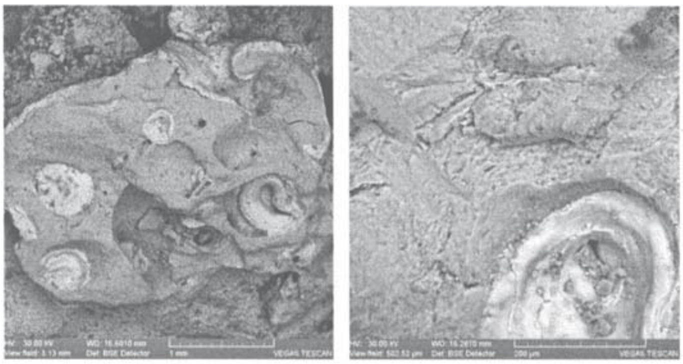


Fig. 7. EDX spectrum in the area of the glazed formations on the fibula with the inventory number 13

Table 1
COMPOSITION DETERMINED FROM THE SPECTRUM SHOWN IN FIGURE 7

Element	AN	[norm. wt.+%]	[norm. at.+%]	Error in %
Iron	26	75.55576	48.77513	2.09862
Silicon	14	3.026896	3.885493	0.194278
Nitrogen	7	0.034413	0.088577	0.11526
Calcium	20	0.688605	0.619434	0.05649
Oxygen	8	20.69432	46.63137	2.966642
		100	100	



a b

Fig 8. SEM image in the bone area: a - 70X BSE, b - 450X BSE detail

The degradation crust from the spring is a discontinuous one with non-uniform corrosion deposits and embedded microstructures from the archaeological site. The Fe, C, Si, Al, Ca, Mg, Na, K, Cl and P elements presented in table 2 on the basis of the spectrum shown in figure 9 can be found in the area of the bone impression at the bone – metal interface (fig. 8, a- b).

The alloying elements resulted from the ore and from the working out of the alloy have an uniform distribution in the microphotograms obtained by the SEM – EDX microscopy (fig. 8, a – b, and fig. 10); in exchange, the microelements and the microstructures resulted from the contamination processes, under the influence of the pedological factors, have zone and concentrated distributions. Thus, there are easily rendered evident the bone impressions by the concentration of the P, Ca and C

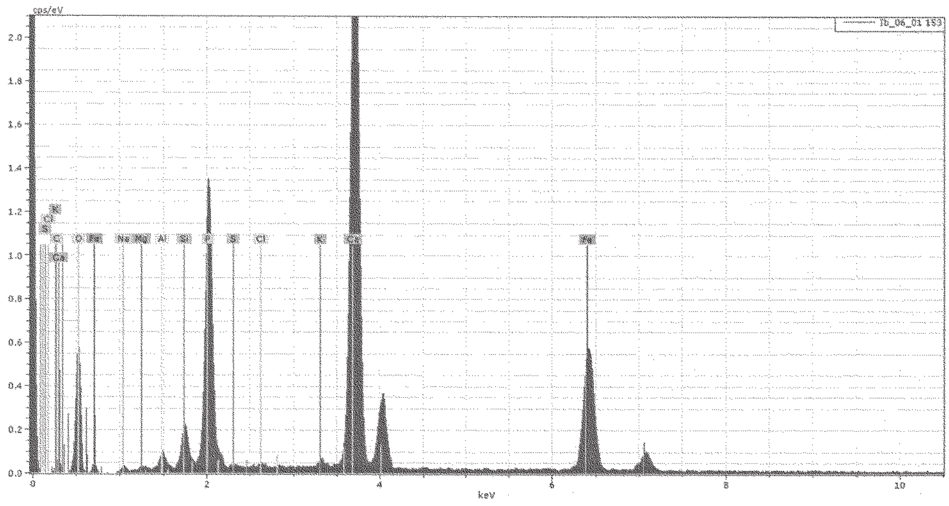


Fig. 9. EDX spectrum in the bone area

Table 2
COMPOSITION DETERMINED FROM THE SPECTRUM SHOWN IN FIG. 9

Element	AN	[norm. wt.+%]	[norm. at.+%]	Error in %
Calcium	20	43.28359	33.32672	1.313232
Phosphorus	15	16.49394	16.43258	0.708141
Iron	26	17.44642	9.640109	0.494389
Silicon	14	2.301645	2.528899	0.147082
Aluminium	13	0.807927	0.924018	0.085178
Carbon	6	0.034118	0.087655	0.365831
Sodium	11	0.396008	0.53155	0.082326
Magnesium	12	0.07189	0.091274	0.039518
Sulfur	16	0.039722	0.038226	0.031708
Chlorine	17	0.096977	0.08441	0.035562
Potassium	19	0.337776	0.266592	0.045499
Oxygen	8	18.68999	36.04797	8.855237
		100	100	

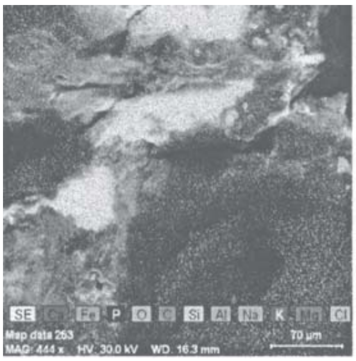


Fig. 10. Element Mapping, 444X

atoms, the silice (SiO_2) presence by zone concentrations of Si and O, caolin by the zone concentration of Al and Si.

Conclusions

During the lying period in the archaeological site the metallic objects are subjected to some chemical, hydrical and microbiological processes influenced by the soil aggressiveness, among these the chlorides having the most important role in the changing of the chemical compositions. The degradation processes after the extraction from the site, e. g. the thermal ones, as a result of burning as well as those which have taken place in the soil (the redox, the chemical and electrochemical oxidations, the acid-basic and the complexation processes through hydration/dehydration) are accelerated by the presence of the oxygen and of the atmospherical humidity higher than 75 % when some inert compounds of the oxydic or carbonate types are passing into Fe (II) and Fe (III) oxyhydroxides.

Initially the changes in the chemical composition are taking place on the metallic surface. This stage is difficult to be detected in the case of the iron archaeological pieces with atypical structures or formations, resulted from thermal or hydrical processes before the burial because the corrosion processes take place in a short time period at a high speed. For instance, the glazed structures resulted from the burning and vitrifying processes undergo in time structural reforming under the influence of the hydrical processes with the keeping to a great extend of the paracrystalline or amorphous formations. In the archaeological sites the objects are discovered in an advanced stage of chemical alteration, partially or completely mineralized. That is why the identification of the external corrosion layer and its chemical composition have an important role regarding the estimation of the processes of chemical alteration during the lying period; these processes are important in establishing the conservation – restoration activities, the type of the physico-chemical processes as well as their duration.

The alteration chemical processes are different for the pieces discovered in sites as compared to those found in cremation urns, these differences being attributed to the anthropic factors which directly influenced the latter ones. The archaeological piece, i.e. the fibula with the inventory number 13 discovered on the Gabăra Hill, Neamţ county, has had an atypical degradation mechanism which has led to the formation of a non-uniform external corrosion layer with discontinuities due to the elements characteristic for the physical deterioration processes (cracks, holes, craters, etc.), due to the deposits of corrosion products resulted from the chemical alteration processes as well as to the formations which induce anthropical influences, more exactly the participation of the object at the burning process before the abandonment time. The analyses with the optical microscopy and with the SEM-EDX have rendered evident the non-uniformity of the external corrosion layer both on the fibula body and on the spring, and the presence of the carbon in the glazed formations allows the mentioning of the anthropical influences before the abandonment time by passing the piece through fire, a process which has been probably accomplished during the burial ritual by cremation. The heat combining of the iron with the carbon has contributed to the appearance in the external layer of some formations which have given the properties characteristic for the alloy and have at the same time influenced the alteration processes during the lying period.

References

1. STAMBOLOV, T., The Corrosion and Conservation of Metallic Antiquities and Works of Art", CL Publication, Amsterdam, 1985, p. 95

2. ROBBIOLA, L., PORTIER, R., Journal of Cultural Heritage, 7, 2006, p. 1

3. ROBBIOLA, L., BLENGINO J. M., FIAUD C., Corrosion Science, 40, **12**, 1998, p. 2083

4. ROBBIOLA, L., HURTEL, L.P., Metal 95, James and James Ltd, 1997, p. 109

5. QUARANTA, M., SANDU, I., Micro-stratigraphy of copper – based archaeological objects: description of degradation mechanisms by means of an integrated approach, 9th International Conference on NDT of Art, Jerusalem Israel, 25-30 May 2008

6. SANDU, I., URSULESCU, N., SANDU, I.G., BOUNEGRU, O., SANDU, I.C.A., ALEXANDRU, A., Corrosion Engineering Science and Technology, 43, 3, 2008, p. 256

7. MAZZEO, R., Patine su manufatti metallici, în Le Patine. Genesi, Significato, conservazione - Kermesquaderni, Ed. Nardini, Firenze, 2005 p.29

8. WAGNER, D., DAKORONIA, F., FERGUSON, C., FISCHER, W. R., HILLS, C., KARS, H. AND MEIJERS, R., Metal 95, James and James Ltd, 1997, p. 21

9. GERWIN, W., SCHARFF, W., BAUMHAUER, R., Metal 98, James and James Ltd, 1998, p. 100

10. MOUREY, W., Conservarea antichităţilor metalice - de la săpătură la muzeu, Ed. Tehnică, Bucureşti, 1998

11. MIRCEA, O., SARGHIE, I., SANDU, I., QUARANTA, M., SANDU, A.V., Rev. Chim. (Bucureşti), 60, nr. 2, 2009, p.201

12. SANDU, I.G., STOLERIU, S., SANDU, I., BREBU M., SANDU A.V., Rev. Chim. (Bucureşti), **56**, nr. 10, 2005, p. 981

13. SANDU, I., DIMA, A., SANDU, I.G., Conservation and Restoration of Metallic Artifacts, Ed. Corson (ISBN 973-8225-24-8), Iasi, 2002, p.143

14. SANDU, I., Deterioration and Degradation of Art Works, **I**., Inorganic Materials Artifacts, "Al.I.Cuza" University Press (ISBN 978-973-703-342-0), Iasi, 2008, p.187

15.URSACHI, V., Carpica I, 1968, p. 111

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