Research on Atypical Formations from Corrosion Bulks of an Ancient Bronze

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Our study focused on the morphology of the corrosion crusts, with a complex structure, resulted during the underground stay of certain shield fragments, dated to the 1st century B.C., the 1st century A.D.. They were made of copper alloys and were found in Brad, the Negri commune, in Bacău county. Our analysis employed non-destructive methods, such as optical microscopy (OM) and scanning electron microscope combined with energy dispersing X-ray analysis (SEM-EDX) and our results revealed several important characteristics with archaeometric potential. We also found a series of atypical structures, such as flat bulbs formed after abandonment, which contained secondary chemical and contamination compounds, as well as a series of chemical congruent surface components, which may be used as archaeometric indicators of the structural crystalline reformation processes that occur during the underground stay period.

Keywords: bronze artifacts, corrosion bulk, primary, secondary and tertiary patina, archaeometric characteristics, OM, SEM-EDX

The use of modern, non-invasive analysis methods (such as OM, SEM-EDX XRD and XRF) for the study of ancient metal artifacts found during archaeological researches, contributed continuously to the development of our knowledge and understanding of the household activities and the organization and communication of ancient populations, as well as to the establishment of the relationships and the commercial, cultural and spiritual links existing in the past [1-12].

Currently, because we needed to know all the aspects in the evolution of humanity, archaeometallurgy became a primary interest for its aspects regarding the acquisition of raw materials, the processing thereof in order to obtain alloys, which were subsequently crafted into objects that were necessary in daily activities, in households, or in agriculture, jewelry items, garment accessories, decorative objects, or rank indicators, cult objects, or commercial exchange units. In that regard, interdisciplinary researches aim to determine those characteristics of an artifact that were preserved and those that evolved in time [13-25], by analyzing the morphology of the corrosion crust resulted from processes of physico-chemical and micro-biological alteration and physico-mechanical deterioration (the internal and external stratification of elements, the nature of the contamination microstructures originating from the soil, the presence of cracks, rifts, or of surface effects, such as flat bulbs, microcrystalline reformed congruent chemical compounds etc.). Additionally, they reveal the heritage elements and functions involved in cultural authentication and integration [26-32].

During the study of ancient metallic artifacts, the corrosion crust is an important source of information in regard to the quality of the alloy and the processing technique, as well as to the degree of wear and aging before and after abandonment. It reveals certain elements regarding the route of an object from its manufacture to its discovery [5-7, 29]. Thus, in the evolution from conception to abandonment of an artifact, it is important to learn the function and the role which that artifact had during its use. For instance, we should learn whether it was part of various activities (agricultural, household activities, battles, decorative activities, etc.) and also to learn how it was abandoned. There are various reasons for abandoning an artifact: the loss of its usage functions (wear, aging), a direct way of abandonment and subsequently the object will lay in and on the ground and funerary practices, by incineration (when the object is stored in urns, or pits) or inhumation (the object is buried underground) [5, 9-12, 27, 31, 32].

The surrounding environment will continue the degradation of the artifact and when it is uncovered it reveals a series of elements characteristic to certain factors and processes that occurred after abandonment (deposits of chemical compounds, soil contamination microstructures, cracks, fragmentations etc.). They may help establish the state of degradation and the measures needed to be taken for preservation and conservation.

Our study focused on the morphology of the corrosion crusts, with a complex structure, resulted during the underground stay of certain shield fragments, dated to the 1st century B.C., the 1st century A.D.. They were made of copper alloys and were found in the archaeological site at Brad, the Negri commune, Bacău county. The objects have a complex load of the external crust and of the bulk - atypical flat bulb structures and primary and secondary chemical compounds resulted by structural crystalline reformation, which are indicators of the chemical alteration processes occurring in the evolution of those objects during their underground stay.

Experimental part

Artifacts and Methods

During archaeological digs performed in Brad, Bacău county [33], were discovered several copper alloy fragments and in order to emphasize the process of chemical alteration and physical deterioration, we will

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focus on the case of certain items with archaeometric potential in interdisciplinary researches of metallic artifacts. There are three U-shaped items and a flat one from the rim of a shield (fig. 1a-c), whose corrosion crusts feature complex surface formations, resulted from the degradation processes that occurred after abandonment of the object.

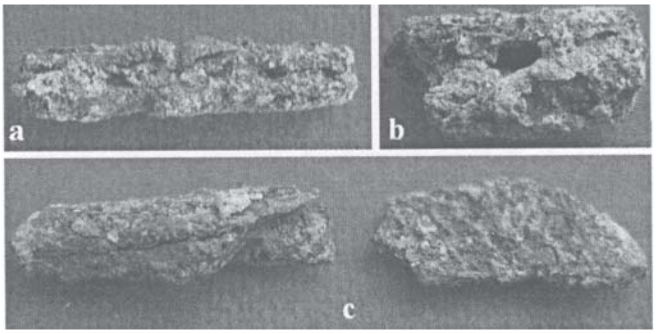

Fig. 1. Shield rim fragments: a – S1; b – S2; c – S3 and S4

For our analyses we used optical microscopy (OM) and SEM-EDX microscopy.

The surface microstructures were studied with an Zeiss Imager a1M microscope, at magnifications of 10X and 200X, coupled to a AXIOCAM camera and using dedicated software.

We used a VEGA II LSH SEM microscope, made by Tescan, The Czech Republic, coupled with an QUANTAX QX2 EDX detector, made by BRUKER/ROENTEC, Germany, to identify the elemental composition and the placement of the microstructures on the surface of items.

Results and discussions

The fragments named S1 and S2 with inventory numbers 12028 and 12029, were shaped as an U from manufacture, but they got altered after abandonment, due to interactions with the environment, to internal and external factors and to processes of physico-chemical and microbiological alteration, but also to physico-mechanical deterioration. Those cumulative processes caused modification in the chemical and physical state of the artifacts, which were almost completely mineralized when uncovered. The corrosion crusts on the items are rough and discontinuous, with elements of physical deterioration, especially cracks and pits, and with unevenly distributed corrosion products of the base alloy and monolithized contamination microstructures from the soil (fig. 2 and 3).

In the SEM image (fig. 4) one can see an area of overlapping physical elements, cracks and crack networks, that compose the corrosion crust on fragment S1, as well as the placement of the corrosion products. According to the EDX spectrum (fig. 4) the elements in the composition of the artifact are: Cu, Sn, Fe and a large part of S, resulted during the processing of the base alloy from polysulphuric ores, while P and another part of the S came from the corrosion crust in the internal profile of the shield rim and resulted from its interaction with the wood and the leather

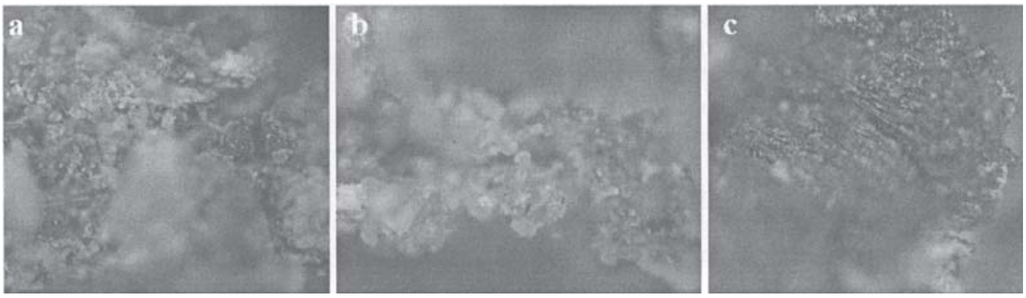

Fig. 2. OM images of surface structures on fragment S1: a - cracks in the corrosion crust (100X) b - secondary chemical compounds (200X); c - microstructures in the corrosion crust (100X)

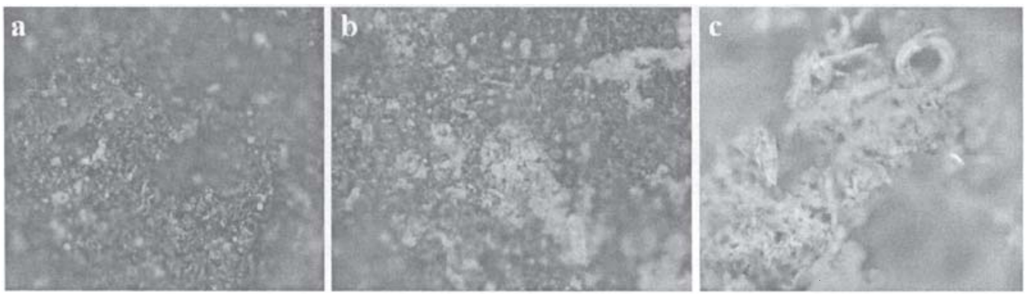

Fig. 3. OM images of surface structures on fragment S2: a and b - deposits of chemical compounds in the corrosion crust (100X); c - crystalline reformed microstructures in the corrosion crust (200X)

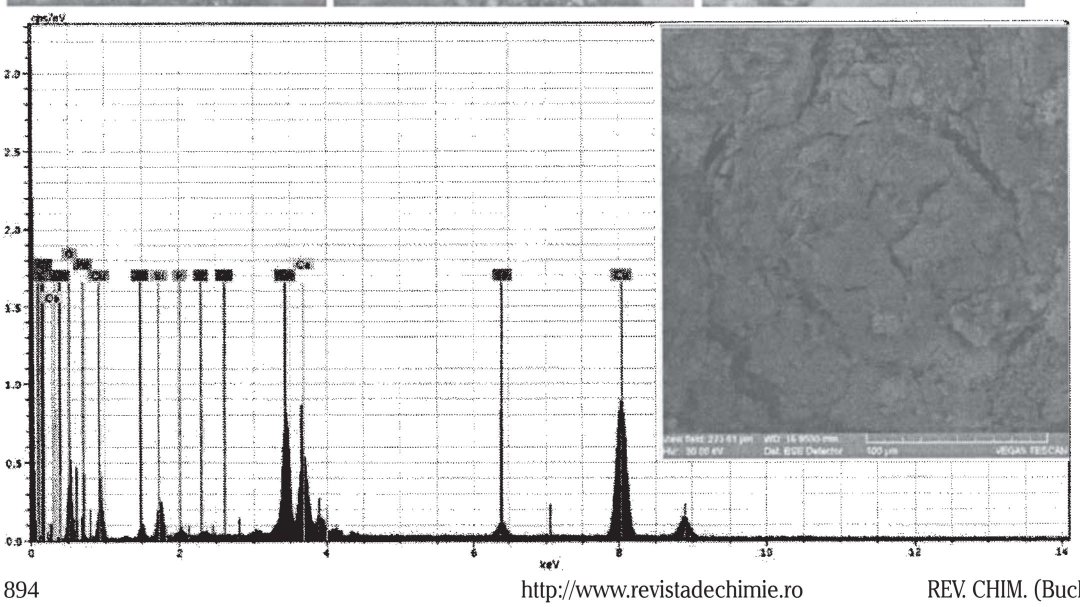

Fig. 4. The SEM image (a) and the EDX spectrum (b) of the corrosion crust of fragment S1; 1000X BSE

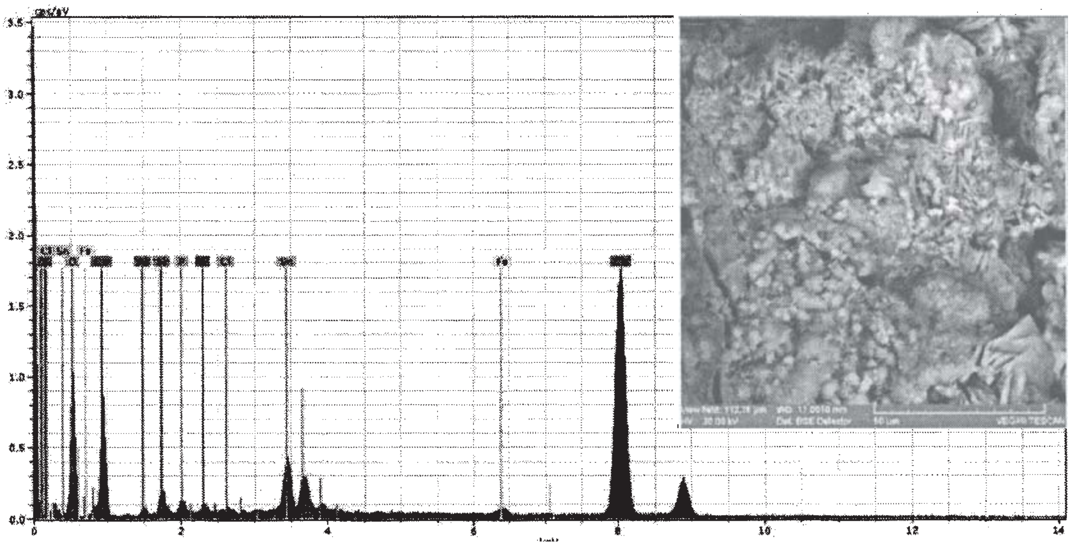

Fig. 5. EDX spectrum and SEM image of the a detailed area on the corrosion crust from fragment S1; 2000X BSE

that covered the wooden plate of the shield. The rest of the elements: Al, S and Ca got included from the soil by contamination, together with Cl and O, which are present in the corrosion crust as chemical compounds structurally reformed on the oxide and base copper carbonate deposits (copper chlorides and hydrochlorides).

Similar SEM-EDX data were obtained for a detailed area on fragment S1 at 2000X, which also revealed, apart from primary and secondary chemical compounds, certain monolithized soil contamination microstructures (fig. 5) The elements revealed by the EDX spectrum in figure 5 are the same as the ones in figure 4, except for Ca.

During the chemical alteration process, the shift of primary to secondary chemical compounds depends on the conditions in the surrounding environment. Thus, the periodical influences of certain external factors (rain, drought, freezing-defreezing, microbiological activities, decomposition of organic matter), together with a series of factors pertaining to the metallic artifact (base alloy and manufacture quality, as well as object wear when abandoned) may lead to interactions that result in the mineralization of the object, that is, a shift to various tertiary chemical compounds: copper oxi and hydroxo-chlorides and base copper carbonates. The flat bulb surface degradation effects on artifacts are atypical among other chemical congruent compounds, as regards their structure, form and size. Such an atypical flat bulb structure was found on fragment S1, resulted from chemical processes occurring after abandonment (fig. 6) and composed of concentric layers that decrease in size from the base to the tip of the bulb. That structure formed due to the Liesegang effect on small areas, where the membrane system consisted of hydroxo- and chloropatites and not of Sn(II), Zn(II) and Pb(IV) hydrogels [5-7].

Fig. 6. SEM image of the formation on S1, 100X BSE

The analyses made around the surface effect also revealed other congruent chemical compounds with granulary structure (fig. 7), the elements identified according to the EDX spectrum being associated with the base alloy (Cu, Fe), with soil contamination (Si, Al, Ca) and with structurally reformed chemical compounds (Cl and O) (fig. 7c).

The SEM image in figure 8 presents the corrosion crust on fragment S2, showing the placement of the chemical compounds resulted from crystalline structural

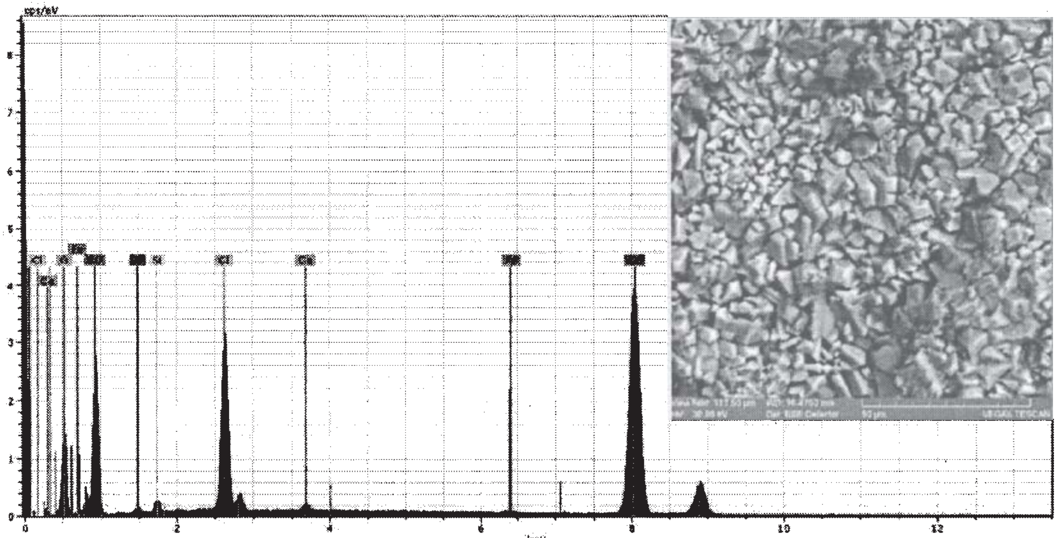

Fig. 7. EDX Spectrum and the SEM image of the granulary compounds in the crust of S1 (2000X BSE)

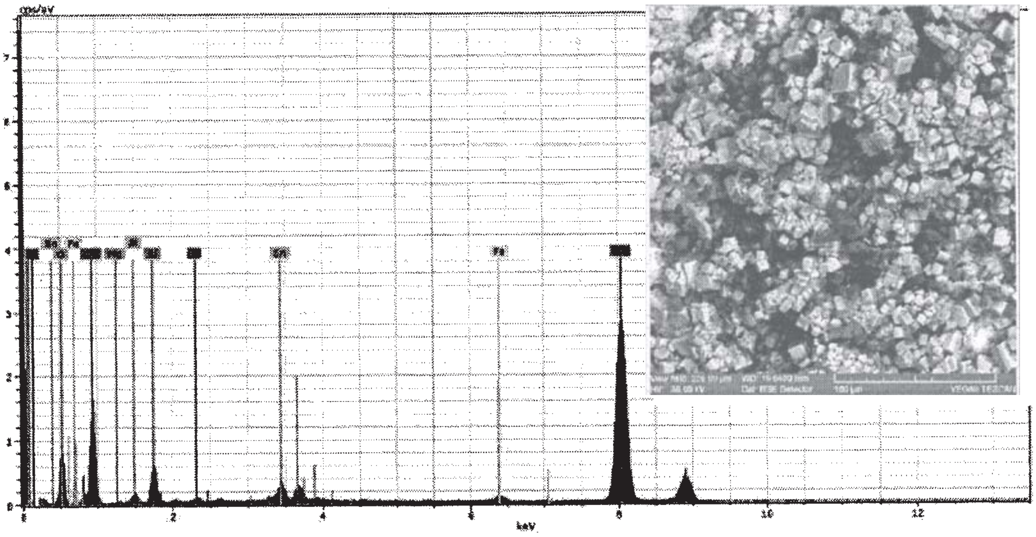

Fig. 8. EDX Spectrum and the SEM image of the corrosion crust of fragment S2; 1000X BSE

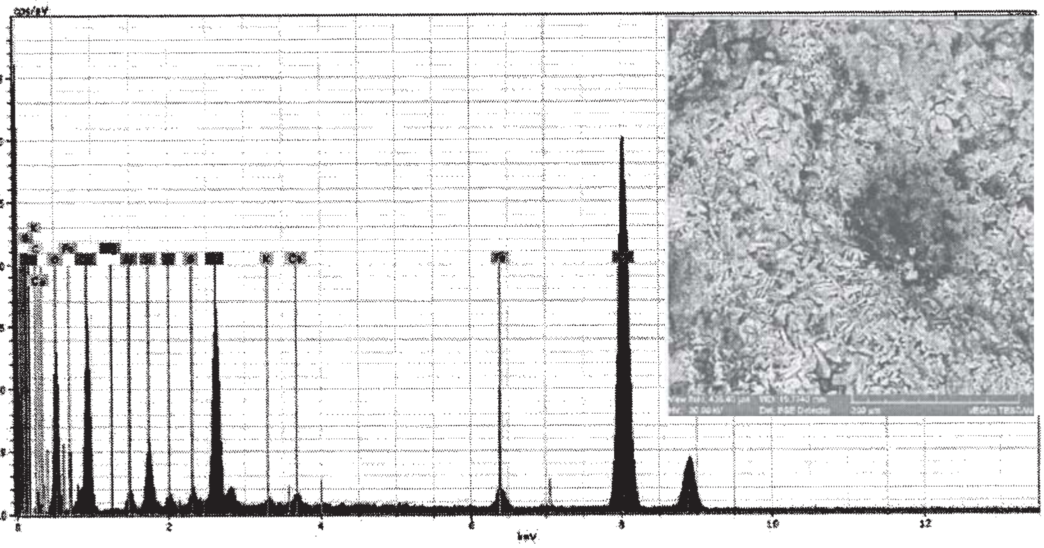

Fig. 9. EDX Spectrum and the SEM image of another area on the corrosion crust of fragment S2, with a different distribution of the corrosion and crystalline reformation deposits, at 500X BSE.

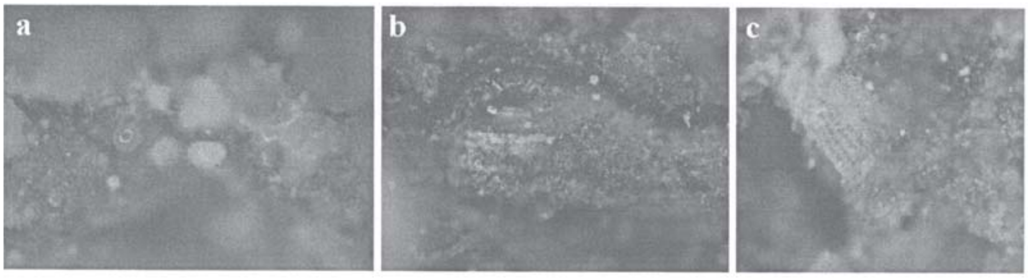

Fig. 10. OM images of surface structures on fragment S3 (200X): a and b - reformed chemical compounds, c - contamination microstructures

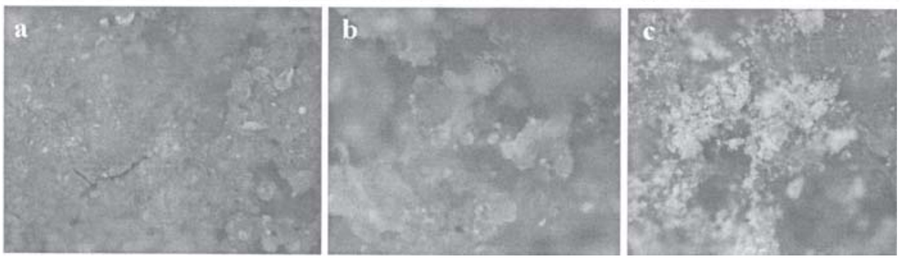

Fig. 11. OM images of surface structures on fragment S4 (200X): a - cracks in the corrosion crust, b - primary and secondary chemical compounds, c - contamination microstructures

reformation. Among the identified elements there are: Cu, Sn, Fe and S, that were in the base alloy (processed from polysulphuric ores), and Si, Al, and Mg, that came from the soil, by contamination (according to the EDX spectrum in fig. 8)

In the EDX spectrum (fig. 9) made on account of the SEM microphotogram, as seen in figure 9, of another area of the S2 fragment, one can see that the element C appeared and part of S and P, as elements from the leather that covered the shield and the wooden part. Moreover, as elements of soil contamination, there are K and Ca, together with Cl and O from the reformed compounds of copper (atakamite and paratakamite). Yet Sn is not present in this area, which suffered processes of segregation.

The fragments S3 and S4, both with 8852 inventory number were part of an item which was broken in two, a U-shaped part (S3) and a flat one (S4). They have rough and discontinuous corrosion crusts, with randomly distributed deposits of primary and secondary chemical compounds. There are visible monolithized microstructures resulted during the underground stay period (fig. 10 and 11). In the section of fragments S3 and S4 a there was a

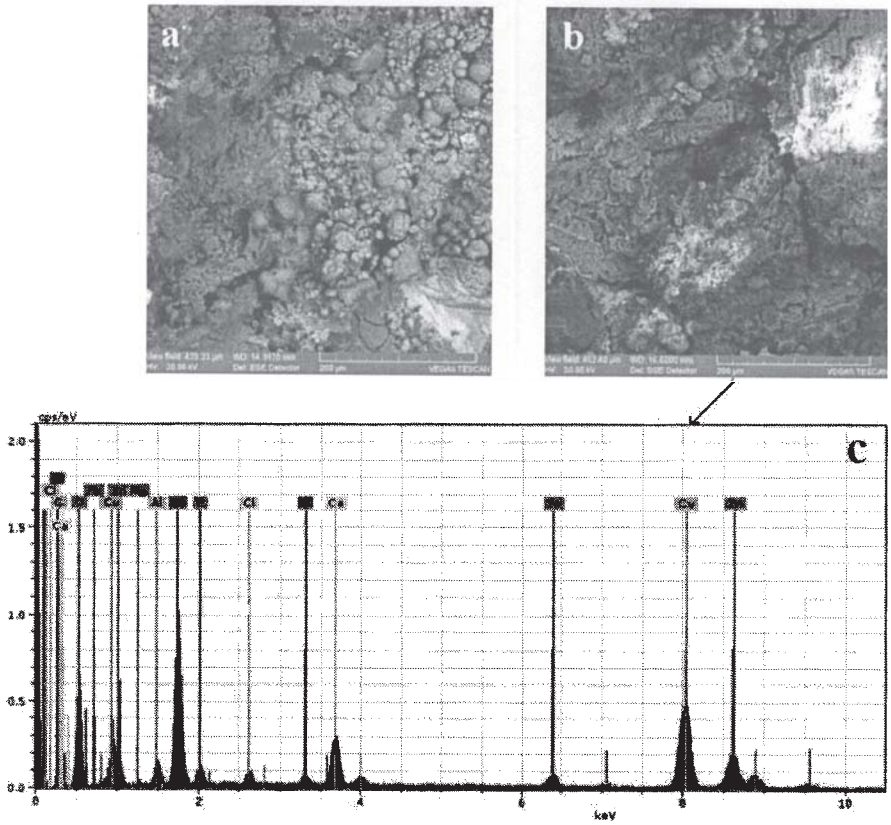

Fig. 12. The SEM image (a and b) and the EDX spectrum (c) of the corrosion crust of fragment S3, for the (b) area; 500X BSE

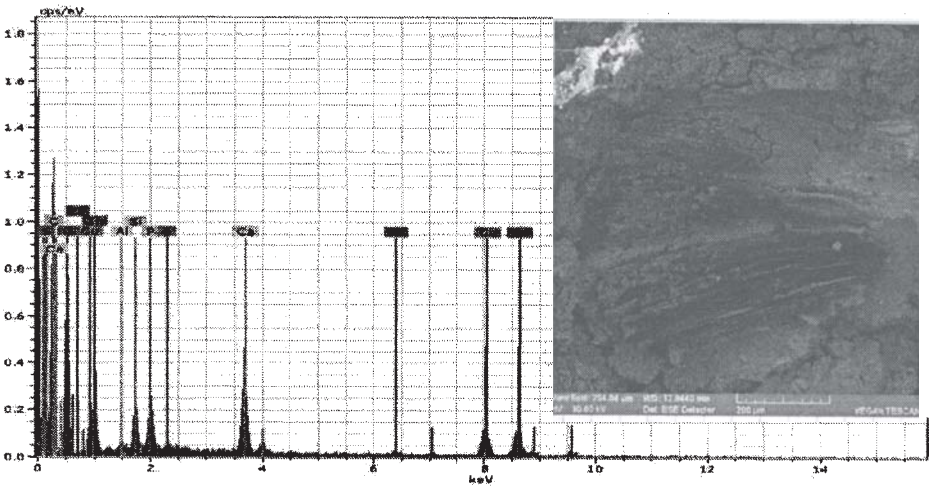

Fig. 13. EDX Spectrum and the SEM image of the corrosion crust of fragment S3; 300X BSE

visible brown-red layer on the metallic core, which was partially covered by a dark green layer.

In the corrosion crust of fragment S3 we identified a series of elements specific to processes of physical deterioration (cracks and pits) and the presence of secondary and tertiary chemical compounds resulted from processes of chemical alteration, crystalline structural reformation and soil contamination (fig. 12a şi b). The elements established according to the EDX spectrum in figure 12c were: Cu, Zn, Fe, which correspond to the base alloy and also those from the soil: Si, Al, Ca, Mg and K, together with Cl and O, which appear in the crystalline structurally reformed compounds. P and C, as revealed by the EDX spectrum (fig. 12c) originated in the interactions of the object with the surrounding environment, the corrosion crust featuring monolithized microstructures and wood fragments.

Moreover, the SEM image in figure 13 revealed a representative microstructure that was assumed to have resulted from the contact of the copper alloy with the wooden plate of the shield, the secondary chemical compounds having conserved those wood fragments well, as they were monolithized. The EDX spectrum in figure 13 revealed the elements in the base alloy, Cu, Zn, Fe and also the soil contamination elements, Si, Al, Ca, as well as elements resulted from the wood and leather parts of the shield, P and S. We should mention that S may originate both from the polysulphurous ore and from the leather, or wood (oak).

Nevertheless, the SEM image of fragment S4 in figure 14, reveals the effects of chemical deterioration: cracks, pits and microstructures in the corrosion crust that are different from those of S3.

The primary and secondary chemical compounds resulted from structural crystalline reformation processes are distributed randomly and correspond to the following classes: copper hydroxoclorides, oxihydroxides and base carbonates. The EDX spectrum in figure 15, corresponding to the SEM microphotogram in figure 15 revealed the following elements: Cu, Sn, Zn, Fe and S, which were in the composition of the base alloy, C, part of S and P, from the leather that covered the shield, Si, Al, Ca, Cl and O,

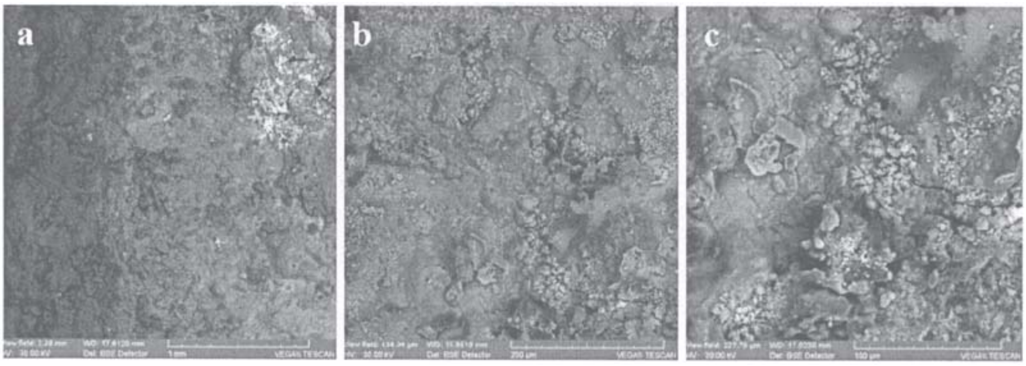

Fig. 14. SEM images of a representative area on the corrosion crust of fragment S4: a - 100X BSE; b - 500X BSE; c - 1000X BSE

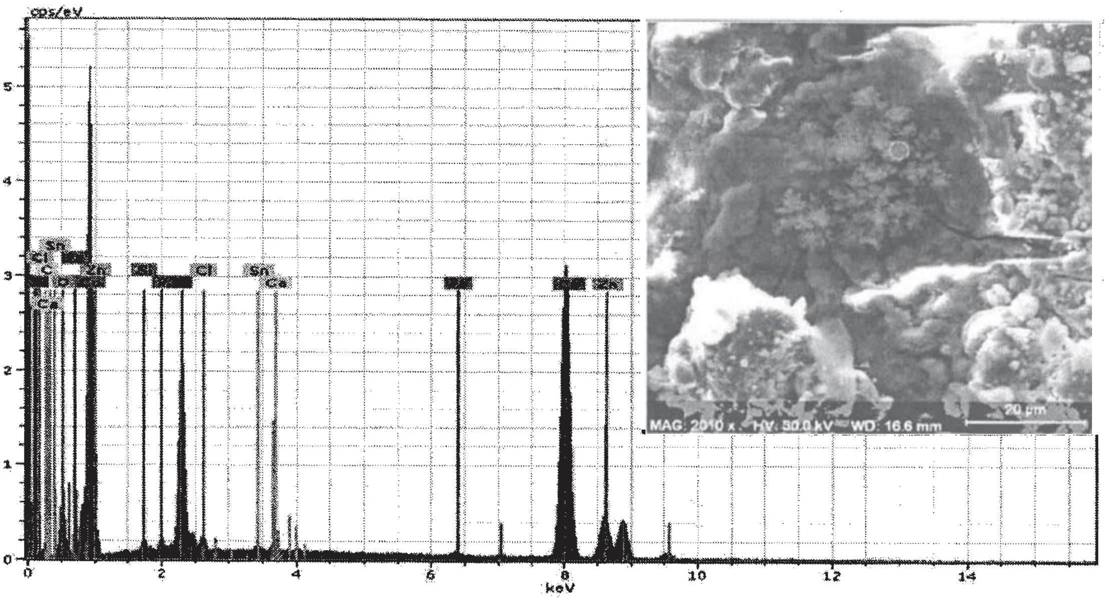

Fig. 15. EDX spectrum and SEM image of a representative area on the corrosion crust of fragment S4

from the soil, the latter two being found in combination with elements in the alloy.

The data above confirmed that the four fragments were parts of the same shield, even if the first two were discovered earlier, but in the same location as the other two.

Conclusions

We analyzed the four ancient bronze fragments of the rim of a wooden shield, initially covered with leather, which were found in the archaeological site at Brad, Bacău county and dated to the 1st century B.C. - A.D. and according to our OM and SEM-EDX data, we reached the following conclusions:

-during the underground stay period the artifact interacted with the surrounding environment, the fragments being partially, or totally mineralized and the Liesegang effect was present on a limited area;

- by EDX we identified the base alloy elements, Cu, Sn, Zn, Fe and S and also a series of other elements, such as part of P and S, which originated from the wooden plate and the leather that were not present as such;

-the Cl, Si, Al, K, Ca and Mg that were identified in the corrosion products, especially in the contamination microstructures, were included from the soil into the crust of the corrosion bulk, as various reformed compounds;

-our data indicates that the four fragments were originally parts of the rim of a shield, the first two being found in 1974 and other in 1971, in the same site, but in different places;

-the last two fragments, inventoried under the same number, are from different parts of the shield.

Acknowledgement: This work was made possible with the financial support of the POSDRU project number 89/1.5/S/63663 and POSDRU project number 86/1.2/S/62307.

References

1. NICKEL, D., HAUSTEIN, M., LAMPKE, T., PERNICKA, E., Archaeometry, 54, 1, 2012, p.167
2. MOHAMED, W., DARWEESH, S., Archaeometry, 54, 1, 2012, p. 175
3. KIRFEL, A., KOCKELMANN,W., YULE, P., Archaeometry 53, 5, 2011, p.930
4. CHIAVARI, C., DEGLI ESPOSTI, M., GARAGNANI, G.L., MARTINI, C., OSPITALI, F., Archaeometry 53, 3, 2011, p. 528
5. MIRCEA, O., SANDU, I., VASILACHE, V., SANDU A.V., Microscopy Research and Technique, 75, 2012, DOI: 10.1002/jemt.22090
6. SANDU, I.G., MIRCEA, O., VASILACHE, V., SANDU, I., Microscopy Research and Technique, 75, 2012, DOI: 10.1002/jemt.22106
7. SANDU I., APARASCHIVEI D., VASILACHE V., SANDU I.G., MIRCEA O., Rev. Chim. (Bucharest), **63**, no. 5, 2012, p. 495
8. SANDU, I.G., STOLERIU, S., SANDU, I., BREBU, M., SANDU, A.V., Rev. Chim. (Bucharest), **56**, no. 10, 2005, p. 981
9. MIRCEA, O., SÂRGHIE, I., SANDU, I., QUARANTA, M., SANDU, A.V., Rev. Chim. (Bucharest), **60**, no. 2, 2009, p. 201
10. MIRCEA, O., SÂRGHIE, I., SANDU, I., URSACHI, V., QUARANTA, M., SANDU, A.V., Rev. Chim. (Bucharest), **60**, no. 4, 2009, p. 332
11. SANDU, I., MIRCEA, O., SÂRGHIE, I., SANDU A.V., Rev. Chim. (Bucharest), **60**, no. 10, 2009, p. 1012
12. SANDU, I., MIRCEA, O., SANDU, A.V., SARGHIE, I., SANDU, I.G., VASILACHE, V., Rev. Chim. (Bucharest), **61**, no. 11, 2010, p. 1054
13. MOUREY, W., Conservation of metal antiques from excavation to museum, Ed. Tehnica, Bucharest, 1998
14. BERNARDI, E., CHIAVARI, C., LENZA, B., MARTINI, C., OSPITALI, F., ROBBIOLA L., Corrosion Science, 51, no. 1, 2009, p. 159
15.ROBBIOLA, L., PORTIER, R., Journal of Cultural Heritage, 7,1, 2006, p. 1.

16. ROBBIOLA, L., BLENGINO, J.M, FIAUD, C., Corrosion Science, 40,12, 1998, p. 2083
17.SCOTT, D.A., Journal American Institute for Conservation, 29, 1990, p. 193
18. ROBBIOLA, L., FIAUD, C., Revue d'Archeometrie, 16, 1992, p. 109
19.ROBBIOLA L. HURTEL L.P., Standard nature of the passive layers of buried archaeological bronze. The exemple of two Roman half portrais, in Metal 95, International Conference on Metals Conservation, eds. I. MacLeod, S. Pennec and L . Robbiola, James and James Science Publishers Ltd, London, 1997, pp. 109-117
20. DOMENECH-CARBO, A., Analytical Methods, 3, 2011, p.2181
21. DOMÉNECH-CARBÓ, A., DOMÉNECH-CARBÓ, M.T., PEIRÓ-RONDA, M.A., Analytical Chemistry, 83, 2011, p. 5639
22. DOMÉNECH-CARBÓ, A., DOMÉNECH-CARBÓ, M.T., PEIRÓ-RONDA, M.A., OSETE-CORTINA, L., Archaeometry 53, 2011, p.1193
23. FJAESTAD, M., NORD, A.G., TRONNER, K., The decay of Archaeological Coopper – Aloy Artefacts in Soil. Metal 95. International Conference on Metals Conservation, eds. MacLeod, I. Pennec S. and Robbiola L., James and James Science Publishers Ltd, London, 1997, p.32
24. GOFFER Z., Archaeological Chemistry, second ed. John Wiley & Sons, New Jersey, 2007
25. SCOTT, D.A., Copper and Bronze in Art, Getty Publications, Los Angeles, 2002..
26. SANDU, I., Deteriorarea si degradarea bunurilor de patrimoniu cultural, vol. I, "Al.I.Cuza" University Publishing House Iaşi, 2008
27. MIRCEA, O., Conservarea pieselor arheologice, Ed. Musatinia, Roman, 2010
28. SANDU, I.G., SANDU, I., DIMA, A., Restaurarea si Conservarea Obiectelor din Metal, Ed. Corson, Iasi, 2002.
29. SANDU, I., URSULESCU, N., SANDU, I.G., BOUNEGRU, O., SANDU, I.C.A., ALEXANDRU, A., Corrosion Engineering Science And Technology, Maney Publishing, 43, 3, 2008, p. 256
30. SANDU, I.G., VASILACHE, V., COTIUGA, V., International Journal of Conservation Science, 1, no. 4, 2010, p. 241
31. MIRCEA, O., SANDU, I., SARGHIE, I., SANDU, A.V., International Journal of Conservation Science, 1, no. 1, 2010, p. 27
32. VASILACHE, V., APARASCHIVEI, D., SANDU, I., International Journal of Conservation Science, 2, no. 2, 2011, p. 117
33.URSACHI, V., Zargidava-Cetatea dacică de la Brad, Caro Trading (Institutul Român de Tracologie), Bucureşti, 1995

Manuscript received: 29.03.2012