Non-invasive Techniques in the Analysis of Corrosion Crusts Formed on Archaeological Metal Objects

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The paper presents experimental results obtained by investigation of copper alloy artifacts from the second and third centuries AD, with multi-analytical non-destructive methods such as optical microscopy (OM), X-ray fluorescence (XRF) and X-ray diffraction (XRD). Studies have sought to determine the characteristics of corrosion crusts (external and internal microstructure of metal alloys, the nature and distribution of chemical compounds, the nature of microstructures and incorporated elements of the archaeological site etc.), that are used in authentication. Corrosion compounds and arrangement of the elements in the upper-coating have contributed to the elaboration of a complex mechanism regarding degradation of the artefacts inside soil, mainly supported by internal, external factors and chemical alteration and physical damage processes.

Components in soil degradation occurs under the action of two complex processes: alteration which is produced by chemical processes (oxidation-reduction reactions, acid-base, complexation etc.) and physical damage (deterioration) arising from defects in processing or wearing out of objects in the past (cracks, crevices, holes) or mechanical processes while lying in the ground (fragmentation, grinding, erosion etc.). Combined action of physico-chemical processes is conditioned by internal factors (endogenous) and external (exogenous) [1,2] and during the lying in the ground time corrosion crusts are formed, which in the case of iron alloys are consisting of primary, secondary or tertiary compounds, the order of their formation being: α-Fe2O3 hematite, α-FeO(OH) goethite, γ-FeO(OH) lepidocrocite and magnetite (inert) Fe3O4.

During the degradation mechanism of bronzes [3-7] can be formed two types of structures: type I – known as the noble patina, formed even on the original surface of the objects, with an important role in preserving metals by passivant action, and type II – formed after destruction of the type I. Corrosion crusts of copper alloys are composed of primary or secondary compounds produced by certain stages of degradation. Copper oxides (Cu2O cuprite, tenorite CuO) copper sulphides and sulphates (covellite CuS, chalcocite Cu2S, brochantite CuSO4·Cu(OH)4), hydrated copper carbonates (malachite CuCO3·Cu(OH)2, azurite CuCO3·Cu(OH)2), copper chlorides (nantokite Cu2Cl3·3CuO·nH2O, paratacamite CuCl2·2H2O) are chemical compounds resulting from corrosion of copper [8-14].

Modern analytical methods applied to metal artifacts of iron and copper alloys from archaeological sites revealed a number of structures, complex and different, some resulting from chemical alteration processes, others the result of physico-mechanical processes. Of scientific and museographic point of view, iron objects degraded in soil contribute to emphasizing the chemical and physical processes that occur according the lying environment. Thus, there are closed environments where the objects have lain long time in ceramics pots or pottery urns, and open environments for artifacts found in layers of culture at different depths in soil profile. Particularly interesting are the metal parts containing into the corrosion crust microstructures corresponding material assimilation from the archaeological site, such as textile, wood, bone, plant remains, shells of mussels (fig. 1-4) etc. [8-14].
Most of the objects with embedded material from the archaeological site were discovered in the tombs of cremation and inhumation from the research of 2nd–3rd centuries AD necropoles, such as the Gabâra–Moldoveni or Vâleni–Botești, both from Neamț county [15–17]. In Gabâra necropolis most graves contained cremation urns, many covered with a lid. Inhumation graves were scattered among the cremation ones [17]. The experimental results showed that the metal artifacts of iron or copper alloys formed during the lying time different structurally and compositionally corrosion crusts. In this respect, the paper presents results from tests of corrosion crusts formed on copper alloy objects from the 2nd and 3rd centuries AD by non-invasive methods such as optical microscopy, X-ray fluorescence or X-ray diffraction.

Experimental part

Optical microscopy
Microscopic observations were made on an Olympus SZ60 stereomicroscope and a stereomicroscope Carl Zeiss Jena at different magnifications.

X-ray fluorescence
X-ray fluorescence analysis were performed with a portable X-SYSTEM INNOVA, anticatod tungsten tube, 35 KV, 40 μA, exposure time 30 s, processing was done with specialized software.

X-ray diffraction
For determining of corrosion products was used a Bruker D8 diffractometer type.

Results and discussions
Artefacts of copper alloys with different conservation status showed that during the lying time occur physicochemical transformations, which are attributed to some deterioration processes (cracking, fragmentation, grinding or erosion) and chemical alteration (redox, acid-basic and complexation reactions). In the archaeological sites were discovered objects that have preserved traces of degradation influences that can be grouped taking into account the morphology of the corrosion layers, as follows: a. objects with a natural patina, b. perishable items with a thin crust on the surface of machined alloy (primary crust), c. objects with a thick crust (secondary) and metal core partially mineralized, d. objects with a rough rind and multiple elements of physical deterioration and mineralized bulk. Figure 5 presents the types of corrosion layers formed on metal objects that have long lain in the soil.

- In the first stage some bronze artifacts form a smooth patina that provides protection to the metal alloy, while K verschiedenartige Hoffnung...
others form the primary crust, which is continuous, with a uniform distribution of corrosion products, but non-protective of metal alloys;
- in the second phase secondary crust are formed by destroying the natural patina or the primary crust;
- in the third phase have been identified objects which have corrosion crusts and untouched metal core;
- in the last phase of alteration process copper alloy is fully converted to corrosion products.

Most of the items discovered in this last phase have not the original form of artifacts, being lost in the archaeological site through erosion and grinding processes.

**Fashion Objects**

Deposits with corrosion products have a zonal distribution, they are more concentrated at the ends of the ring (fig. 6). Elemental composition determined by X-ray fluorescence spectrometer is as follows: 98.97% Cu, 0.74% Fe, 0.29% Pb, according to XRF spectrum of figure 7.

Fibula. A special situation was encountered in objects whose parts are made from different metals superimposed. In fibulae made of two metals, such as fibulae resorts, corrosion crusts consist of byproducts resulting from corrosion of both metals. As was the case of clothing accessories, namely fibulae with copper alloy body, while spring was made of an iron beam with turns of copper alloys wrapped around.

Crust morphology of the spring with fibula is different from that formed on the body, in the composition of the outer layer being located both byproducts of corrosion of copper and iron ones.

Elements determined by X-ray fluorescence on the body and spring are shown in table 1, according to the spectra in figures 8 and 9.

Figure 10 shows XRD diffraction spectra obtained for the fibula, in which there is evidence of primary and secondary chemical compounds of copper and compounds embedded in the soil, such as quartz and calcite.

**Table 1**

<table>
<thead>
<tr>
<th>Elements</th>
<th>On the body</th>
<th>On the spring</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>93.39 ± 0.43</td>
<td>84.05 ± 0.59</td>
</tr>
<tr>
<td>Fe</td>
<td>0.64 ± 0.04</td>
<td>11.34 ± 0.20</td>
</tr>
<tr>
<td>Zn</td>
<td>5.67 ± 0.11</td>
<td>2.98 ± 0.12</td>
</tr>
<tr>
<td>Pb</td>
<td>0.30 ± 0.05</td>
<td>1.56 ± 0.14</td>
</tr>
</tbody>
</table>

The process of physical deterioration and chemical degradation of the artifacts that have components from two different metals, one easily corroidable, like iron, is conditioned by anthropogenic influences and a number of parameters that have altered the internal structures before leaving. Wear, thermal processes, temperature and time that have undergone combustion, materials that were in contact during/after burning etc., have directly influenced the process of change during the lying time. Therefore, some clothing accessories of fibula type found in cremation graves have discontinuous corrosion crusts, rough, with irregular structures embedded in materials by monolithing.
Fibula spring has the corrosion crust composed of layers, the outer layer being open-green and having elements of processes of deterioration (fig. 11), such as voids, exfoliation of thin sheets, head erosion (fig. 12 a and b).

Corrosion crust contaminated following the interaction with iron artifacts from the archaeological site was revealed by analysis with X-ray fluorescence spectrometer. Elements determined are: 77.48 ± 0.85% Cu, 4.37 ± 0.20% Fe, 14.89 ± 0.38% Zn, 1.58 ± 0.25% Ag, 1.69 ± 0.23% Pb, as shown in XRF spectrum (fig. 13).

Chemical compounds resulting from chemical alteration of copper process were put in evidence by the X-ray diffraction: ortorombic crystallized chlorides and copper sulfides (fig. 14).

In general, noble patina is identified on the surface of bronze objects, appears as a smooth film of different colors: blue, green, dark green, metallic gray. Fine look of the patina and protective qualities make it to be called “noble patina”. Corrosion appearance is a consequence of internal oxidation and leads to the formation of corrosion crusts.

Primary crust is on the outside of metal artifacts resulting from the oxidation of metallic copper through copper oxide formation, especially cuprite, Cu2O. Cl ions presence lead to copper chloride presence, which was highlighted both at weakly altered pieces as well as at the mineralized ones.

The primary crust has an uneven distribution of chemical compounds, following point-shaped corrosion, or even following generalized corrosion. Both the uniform and the uniform crust are permeable to water and oxygen, while metallic copper will rise by oxidation new copper compounds, such cuprite.

Secondary crust is formed by the action of complex processes of chemical alteration and physical damage,
through which metallic copper become primary, and simultaneously occur reforming crystalline structure reactions, the primary compounds passing into the secondary. This secondary crust is composed of sulfides, hydrated basic carbonates and copper chloride. Secondary crust has been seen in partially/totally mineralized parts, respectively at the the bulk interface with/without metal core.

Conclusions

Scabs or outer layers of metal artifacts are characterized by chemical compounds (primary or secondary) and their arrangement from point-shaped or general corrosion processes, respectively lamellar, intercrystalline or transcrystalline.

Based on processes of chemical alteration, continuous corrosion crusts are formed (general corrosion), or discontinuous (selective or punctate corrosion).

Defects in processing and metal artifacts wear (cracks, scratches, debris from processing etc.) contribute to the formation of discontinuous crusts.

Homogeneity/inhomogeneity of corrosion scale is related to the presence of microstructures embedded in the metal core in the archaeological site.

For parts in the cremation graves, the anthropogenic factor, by combustion processes which are subject to prior abandonment, significantly affects the mechanism of their degradation in soil.

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