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STUDY ON THE SPECIFIC EFFECTS OF CORROSION PROCESSES ON ANCIENT BRONZE ARTEFACTS

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ABSTRACT

The paper presents the cases of the corrosion processes which take place on starting from the usage period when the primary patina is being formed and when the secondary patina starts, than continuing with the archaeological site where the contamination patina is obtained under the influence of the pedological processes. The paper is a review from the specialised literature and from the contributions of the authors. There has been used the direct analysis with optical instruments, electron microscopy and EDX.

KEYWORDS: corrosion products; primary, secondary and contamination patina; ancient bronze artefacts; Liesegang effect; perturbed and non-perturbed archaeological sites.

1. Introduction

Metals, as compared to other materials, have a unique behaviour after the creation of artefacts, such as *high resistance* to exogenous factors, *returning to the primitive state of mineral* through the processes of corrosion and erosion [1-4].

Among the Cultural Heritage assets, the ***coins*** and other metallic numismatic pieces offer many *case studies of the conservation state* and, in the research field, they can be adequate samples to be used for experiments, but except for the *treasures*, the coins are not always easily discovered by excavation if dispersed in the archaeological sites [2].

Except for the *treasures* made of noble metals, the pieces made of other metals have the disadvantage of a precarious conservation state, in the worst case of ***pre-collapse*** – as the pieces with a very thin metallic bulk that merely preserve their shape – or of ***collapse*** – when the metallic bulk is completely absent and the shape cannot be recognized, their authentication being almost impossible [1-6]. Among these, the pieces made of ***ancient bronze*** have a *very complex composition* of the corrosion products, resulted from the reactions with the *corrosion agents* (of chemical, electrochemical or microbiological natures, respectively), or by *contamination*, during the various *pedological processes* (*segregations, cementations - monolithisations, re-crystallizations*, etc.). The most important problems arise for the *pieces without metallic bulk*, pieces which during the *preliminary classification* in the yard (excavation place) have been destined to the ”*grey fund*”, abandoned in the most cases.

These pieces are a very important source of information, mainly about the basic mineral, often being the unique proofs of a technique or metallurgical tradition/period [7-11].

Thick corrosion crusts on artefacts fabricated from copper, bronze or other copper alloy may display complex structures. Some of these structural details may be dependent on the microstructure of the metal, which is attacked by corrosive agents during burial. Their formation may also be influenced by a variety of growth mechanisms relating to the development and morphology of the corrosion products themselves [12].

Some papers of interest concerning this subject have been published: unusual phenomena in the corrosion of ancient bronzes are reported [13]. The particular observations of interest here are those concerning the periodic or banded layers of corrosion which are sometimes observed in the polished cross-sections of ancient copper alloys [14].

The origin of the banding which is observed in some archaeological material may be the result of the slow diffusion of metallic constituents and of the salts present in soil groundwaters. So there are a series of reactions that produce precipitation of relatively insoluble corrosion production, such as: cuprite, malachite, atacamite and paratacamite, tin and lead oxide and also other products, which may be present in segregated or banded layers.

Some of the segregation effects which are observed are due directly or indirectly to microstructure-related segregation, such as are observed in dendritic castings, or in multi-phase alloys. Rhythmic banding, however, is not normally explicable as a consequence of the initial metallographic structure of the artefact concerned.

The formation of these periodic structures are based on Belousov-Zhabotkinskii type oscillant reactions of precipitation in heterogeneous phase, which holds the name of Liesegang phenomena or effect [14]. Many studies of this intriguing phenomenon have been made and a number of different mathematical models advanced to explain the precipitation processes [15 - 17]. The stratification of corrosion products, which is formed during burial, it is based on complex processes with cumulative effects, as are: electrochemical processes, template/coordination processes, microbiological processes, fossilisation (mineralisation), segregations, diffusions, etc.

Bronze and brass artefacts present specific cases of the conservation state resulted both from the usage period and after abandon.

These specific effects have interested many researchers during the years. These effects have been studied in order to determinate the formation mechanism or the archaeometric characteristics.

In general, the specific effects are based on complex corrosion processes of old bronzes and brasses which take place inside or at the surface.

This paper reviews some of already published specialized literature on these phenomena, with some notes regarding to the contribution of the authors.

2. Surface Effects

According to the previous studies [1-6], ancient bronze objects, both the ones with metallic bulk and the ones without it, coming or not from perturbed sites, three types of products can be differentiated in the structure of the *archaeological patina*: the first ones resulted from the corrosion processes, the second ones from the acid-base processes, mainly through hydrolysis and ionic exchange, and the third ones from the processes of contamination (diffusion, segregation, deposition, etc.). These products are formed in different stages, being characteristic to certain types of patina.

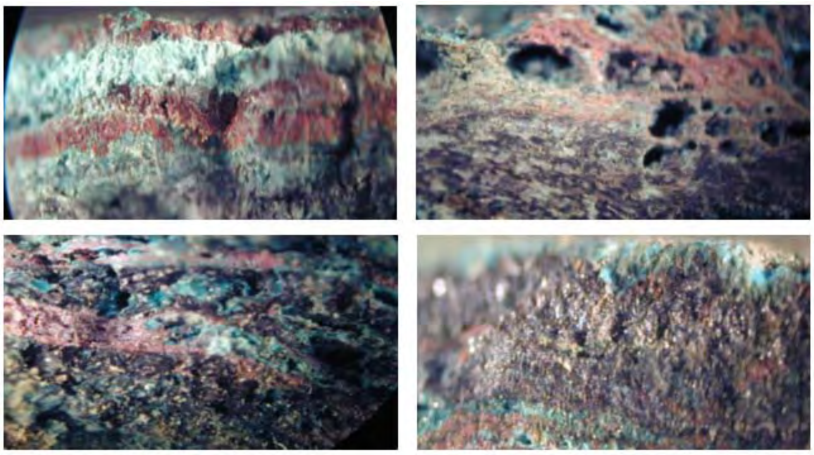
The oxides and sulphides, formed since the usage period, constitute *the primary patina*; the hydroxyhalogenides, oxyhydroxides, carbonates, sulphates, phosphates, etc., resulted in the last period of utilization (before abandon) and in the first step of the pedological period, define the *secondary patina;* finally, those resulted from the physical processes of diffusion-segregation-recrystallization-deposition-monolithisation-mineralisation are forming the *contamination patina* [3, 4].

The study of these products allows not only the explanation of the inner mechanisms of formation but also the evaluation of some archaeometric parameters which can point out some elements useful for authentication, such as the nature of the alloy, the type of the mineral, the technology (the elaboration of the alloy and of the coin), the provenience of the coin (the period and place of creation), the way and the period of utilization and some other data concerning the “time imprint” [4, 7].

The continuous stratigraphical depth of the site in time, from the surface where the action of the climatic, microbiological and anthropological agents is strong and cyclic, towards the internal zones where the aerobical or anaerobical conditions of the soil alternate and the oxygen and water in soil have oscillations in time creating another different system of cyclic variation, has a very important role in structuring the corrosion products, the ionic exchange or the contamination products.

The last cyclic processes, although occur with a very slow rate during the centuries, produce important structural modification of the ancient patina of an object, creating a stratigraphical distribution of the three groups of products. The cyclic properties of the pedological processes determine the specific stratification of the three patinas which can be easily rendered evident by means of the known stratigraphical methods.

If we compare the micro-stratigraphies of the archeological patinas of two coins coming from different sites - one non-disturbed and with low and almost constant humidity, the other one situated in an area with a great mobility of subterranean water and a complex chemistry - we notice the stratigraphical distribution under the form of deposits of products specific to the three types of patina: primary, secondary and of contamination, Fig. 1a [7], for the first coin and a deposition of micro-crystals, not uniform in the volume phase of the archaeological patina for the second coin, Fig. 1b [3, 4].



a ***b***

Fig. 1. *Micro-stratigraphical structure of the archaeological patina [3, 4]: a – patina for coin coming from archaeological non-disturbed (non-perturbed) site and with low Humidity, b – patina for coin coming from archaeological site with a fluctuant chemistry produced by the abundant subterranean water.*

If in the case of a non-disturbed site, we can easily draw up the structural phenomenological correlations for the chronological valuations, for the second one, the study of the parameters implied in such correlations requires either some complex analyses with the help of the co-assisting systems or the corroboration of new methods and techniques of high resolution.

So, the stratigraphical morphology of the most archaeological patinas of the ancient bronze pieces has a *sandwich* structure, characteristic to the *Liesegang effect*, [7] in which the layers of primary patina are overlapped or partially interposed with the ones of the secondary patina. The layers of contamination products, formed during the chemical chronological processes that occur in the heterogeneous liquid-solid systems, with a sequential formation of products with characteristic morphology, are also named the "*Liesegang rings*". In the case of the bronze coins, the primary patina contains layers of *oxydes* and *sulphides* (*cuprite* or *cuprite/tenorite*), the secondary patina of *malachite/azzurite,* overlapped or alternated with layers of *atacamite/paratacamite and brochantite/anthlerite* and of contamination products such as the *ankerite, gypsum, silicates and caolinite* interposed with *cassiterite*, resulted from the segregation and the diffusion processes in the inferior layers [3, 4, 8-11].

If the inner effects are well determined by cross-section analyses, the surface ones can be observed directly or through optical devices as microscopes and stereomicroscopes.

Some authors [18] studied the of surface of archaeological artefacts and effects and grouped them in the following groups: the "even" surfaces, pits or crevices and "coarse" surfaces (Fig. 2).

The "even" surfaces can have extended monochrome areas, easy to identify by mineralogical analysis, but also small areas polychrome and non-uniform.

These surfaces can have dominant colours specific to primary patina compounds (red, brown and green-grey) and few from secondary patina (blue, green, brown, grey bright to dark), with even and bright aspect.

Pits or crevices have as cause the stress from physical and mechanical effects on cracks produced by inter-crystalline corrosion and some inclusions from casting.

The "Coarse" surfaces could have different types of representation: lamellar plates; limpets or buboes (nodules) effect (mono- or polychrome); crust (thick or thin); cracks;

From the study of some ancient bronze coins, made by our collective, some surface effects were identified, not enough studied till now (Fig. 3).

Among the buboes and limpets effects, we discovered dislocation effect through dissolution of the buboes or nodules braking, resulting large round holes.

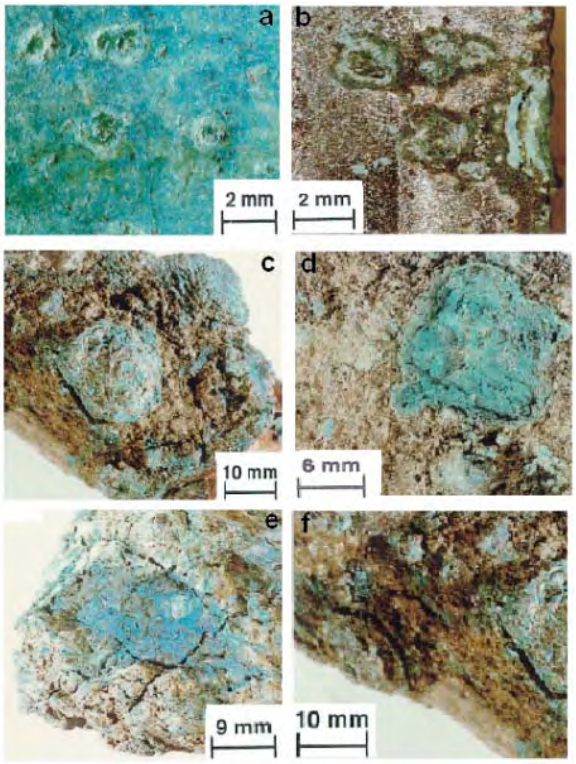


Fig.2. *Macroscopic views of archaeological bronzes dating from the Bronze Age (1500-750 BC) [18]: a – pits and pitting caps; b – lamellar plates; c - buboes (nodules); d – thin crusts; e – cracks; f – crevices.*

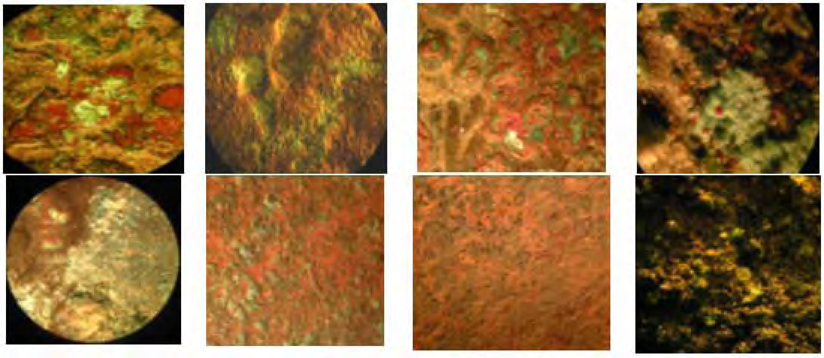


Fig. 3. *Microscopic view of some bronze Austrian and Romanian coins (1880-1888 AC) [3, 4]*

Copper products can form deposits according to the corrosive context:

- hydoxychlorides in seawater;
- hydroxysulphates in the outside environment;
- phosphates, sulphides and silicates from soil;
- hydroxycarbonates elsewhere.

They are described in the literature as corrosion or barrier layers, films and crusts.

They could be formed at any time in the life of the object, so they may possibly carry imprints of its earlier life. For example, it has been noticed that some copper deposits have mantained vegetal or animal fibre structures. Even insects have been noticed and described. This last point is of primary importance and remains to be developed; meanwhile, it is important to continue to look for such traces. The archaeology of the corroded surface could prove to be a source of new criteria for classifying and estimation of the mechanisms.

The formation of the secondary patina has as a first step the transformation of cuprite and chalcokite in malachite, azurite, atacamite, paratacamite, antlerite, brochantite and nantokite (Fig. 4). There have also been identified macrocristalline surface formations with different arrangements (Fig. 5).

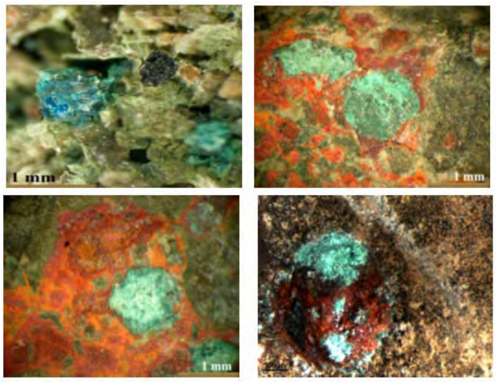


Fig.4. *Optical images that show the first stages of the bronze disease occurrence that seems to start from cuprite nodules and layers [21].*

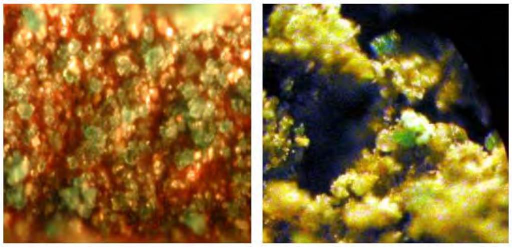


Fig. 5. *Malachite and azurite structures on bronze surface [3, 4]*

3. Inner Effects

Consequently soil elements incorporation is of major importance in the achievement of the final colour of the surface, whereas the dissolved amount of copper due to the selective dissolution is not characteristic of a given aspect of the patina. Robbiola [18] describes two types of deviations from the basic structure. ***Type I*** has other three kinds of deviations. The first is characterized by the presence of a porous external crust or deposit (often several hundred of μm thick) covering the outer layer, the latter sometimes being less developed than in the case when no crust is present. Analysis of such deposits revealed mainly copper corrosion products, such as cuprous oxide (cuprite) and/or cupric compounds, such as hydroxycarbonates or hydroxysilicates and even including sand.

The two zones - top layer (crust) and outer layer - are usually easy to distinguish. For example, on the left of Figure 6-a, the green and brown deposit hugs the concave curve of the engraved decoration, revealed here by the blue-green outer layer.

The interface between this kind of crust and the underlying layer corresponds to the original surface. The external porous deposit is clearly linked with the precipitation of dissolved copper cations onto the surface.

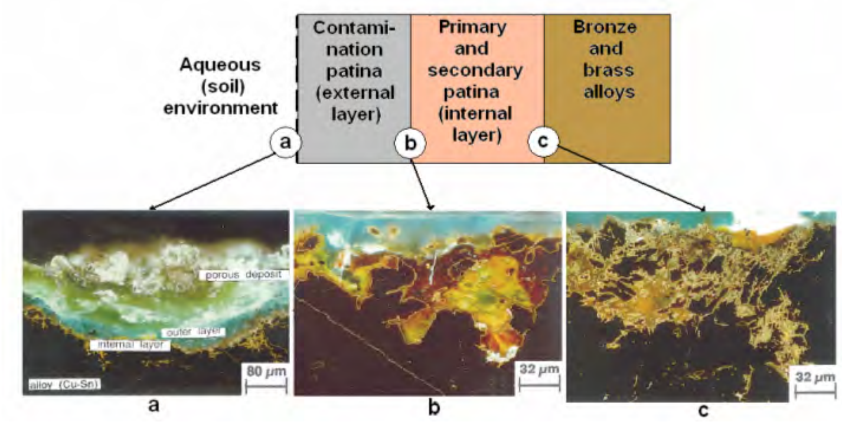


Fig.6. *Type I corrosion structures the three kinds of structural deviations from the basic structure (optical microscopy in dark field: the alloy appears in black) [18]: a – deposit of copper compounds on the outer layer; b – localised atack or crack within the basic structure; c – internal atack of the corrosion/alloy interface.*

The second kind of deviation Figure 6-b corresponds to modifications of the structure due to either localized extension of the inner layer into the alloy or internal cracking. The extension of the internal layer is accompanied by the incorporation of corrosive species, such as chloride anion, which plays a prominent part in localized corrosion (orange zone in Figure 5-b) Cracking can be attributed to many causes, such as internal stresses inside the corrosion layers or ageing of the corrosion products.

The third kind of deviation (Fig. 6-c) corresponds to inter- or transgranular attacks at the layer/alloy interface, ascribable to internal oxidation processes along diffusion short-circuits (possibly due to the presence of defects in the grain boundaries or even to the metallurgical structure itself, as it could be the case for hammered metals).

Type II coresponding to coarse surfaces, results from localized corrosion phenomena, but also from generalized attacks due to a high dissolution rate. In both cases, paradoxically, they show a similar structure and the same distribution of the chemical elements into the corrosive structure. The main characteristic is the presence of high chloride amounts at the internal layer/alloy interface. It appears already that, in contrast with Type I structure, the formation of the internal corroded layer is linked to an enrichment of the corrosion products in chloride anions issued from the soil.

Type II surfaces are rough and their colour may be red, brown or more often green. They fall into two different classes for which, contrary to the structure of Type I, the original surface is not left untouched:

- areas on which corrosion deposits – buboes (Fig 2-c), crusts (Fig 2-d) hide the original surfaces;
- zones on which the original surface of the artefact is clearly destroyed, with loss of matter - pits (Fig. 2-a), crevices (Fig. 2-f) or lamellar plates (Fig. 2-b).

Examination of cross-sections of artefacts shows that all types of Type II corrosion patterns are very close from a structural and chemical point of view. The alterations are often well developed and they are typically 200 μm to several μm thick, depending on the severeness of the attack.

The microstructures displayed in Fig. 9-b and c show that such deposits, whatever their shape, are constituted by a superposition of three layers schematically represented in Figure 7-a.

- an external altered zone of green Cu(II) compounds;
- a red layer of cuprous oxide, often disrupted or fragmented;
- an internal layer, with different possible colours (yellow, orange, brown) characterized by lower copper amounts and relatively higher tin contents than in the alloy, associated with soil elements (mainly O and Cl).

The second kind of deviation results from intensified localized attacks, leading to zoning inside very thick internal layers as in Figure 7-d or to highly developed inter- or transgranular corrosion (Fig 7-e).

The formation of complex stratified corrosion layers has sometimes a periodicity, leading to a complete mineralized structure, such a phenomenon has already been observed, as described by Scott [10,12] for Egyptian artefacts, or by Robbiola [20] for Bronze Age artefacts. The interest for the complex structure of bronze corrosion products leaded to a European Partnership [21]. They have studied the ancient bronzes from the Mediterranean Area. In Fig. 8 – 15 are presented some cross-section with uncommon and commonly observed cases of corrosion of Cu-base archaeological artefacts.

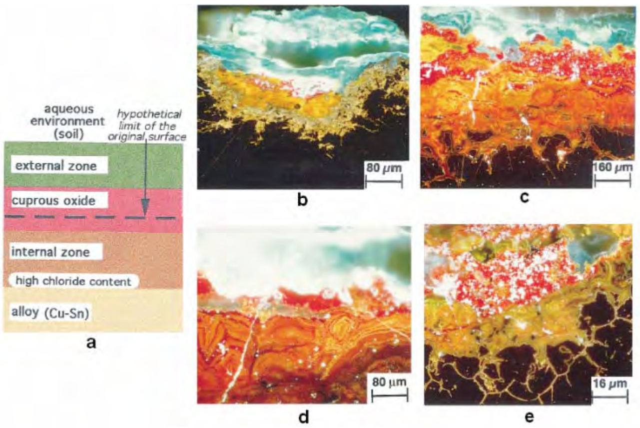


Fig. 7. *Type II corrosion structures (coarse surfaces) characterized by the loss of the limit of the original surface (optical microscopy in dark field: the alloy appears in black) [18]: a – schematic representation of the structure; b - transversal section of a pit; c - transversal section of a thick crust, d and e - details of the internal altered zone under the red cuprous oxide layer; d - is a detail of b showing a thin disrupted cuprous chloride layer up to the internal zone where „ghost" structures of the alloy are still observed; e - shows a pit with intergranular corrosion - the blacks spots in the internal zone in yellow-brown are „ghost" sulphide inclusions remnants of the initial alloy.*

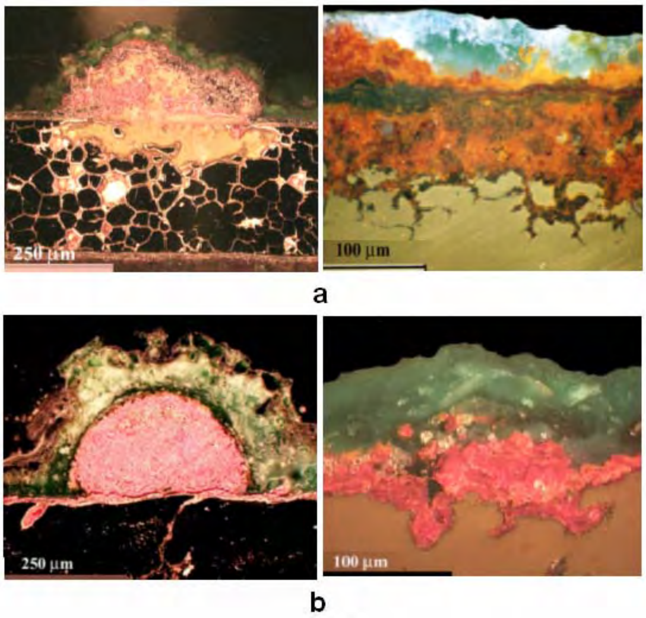


Fig.8. *Optical images of cross sectioned ancient patinas grown on archaeological artefacts during the long-term burial (a) and the artificial corrosion products layers grown on the reference Cu-based alloys by using the $CuCl_2$ method and subjected also to a burial (b). It is possible to identify distinctly different layers in the corrosion products whose location, structure, nature and composition are similar to those observed for archaeological artefacts [21].*

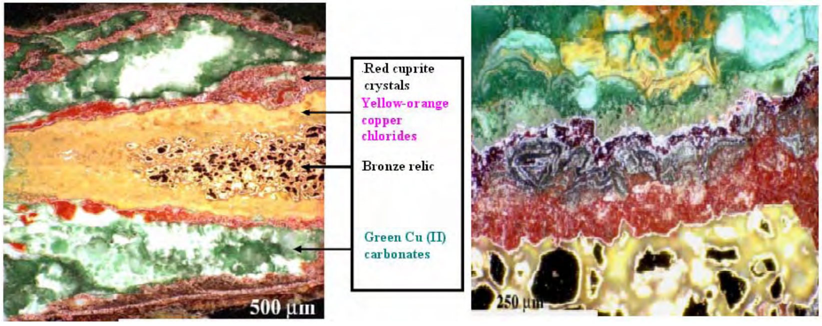


Fig.9. *Optical images that show the complex nature of the stratified corrosion products. The dark spheroidal areas are constituted by the surviving metal (dark field observation) [21].*

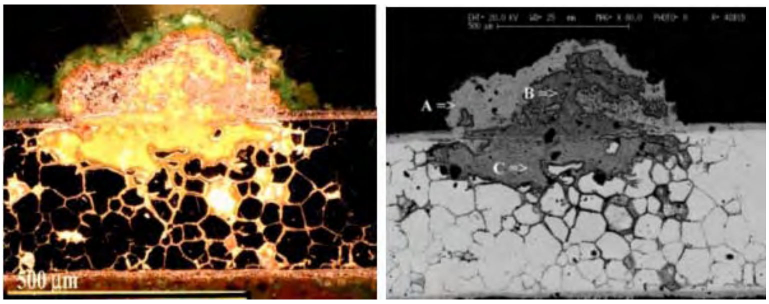


Fig.10. *Typical aspect of cross sectioned archaeological artefacts where erupting cuprite nodules are present. The images show that cuprous chloride (yellow-orange layer) is present at the interface between external corrosion products and metal relic and where also bronze disease is occurring as shown by optical (dark field) and electron images: A – $SnCl_2$; B – Cu; C – $CuCl_2$ [21]*

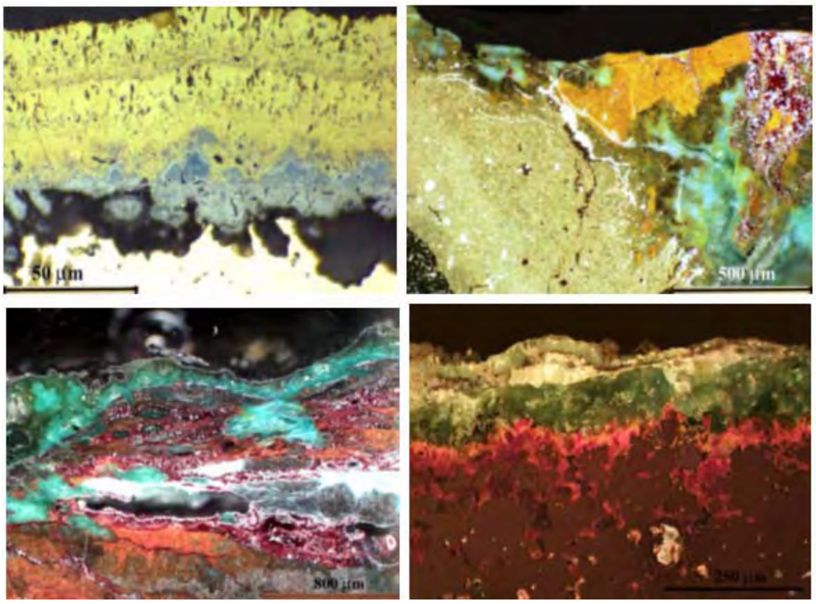


Fig.11. *Uncommon and commonly observed cases of corrosion of Cu-base archaeological artefacts that have induced the formation of complex compounds. The patinas are composed by copper-iron sulphides, pyromorfite, cerussite, azurite, malachite, leadhillite, cassiterite, cuprite and copper chlorides [21]*

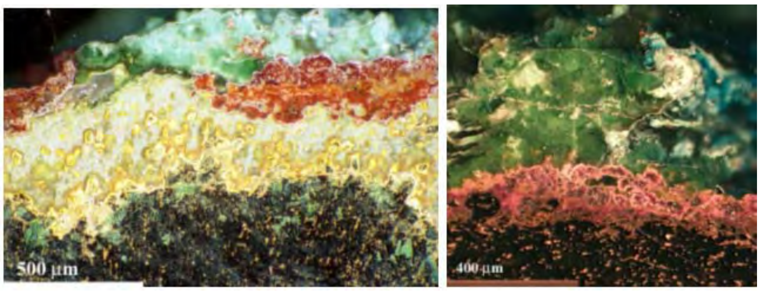


Fig.12 *Optical images obtained from two different areas of the Roman coin. The image on the left discloses the first stages of the so-called bronze disease and the second column evidence the protective role of the copper (II) compounds and of the cuprite that impede the occurrence of the bronze disease. This information demonstrates that the conservation materials and methods must locally inhibit chlorine [21]*

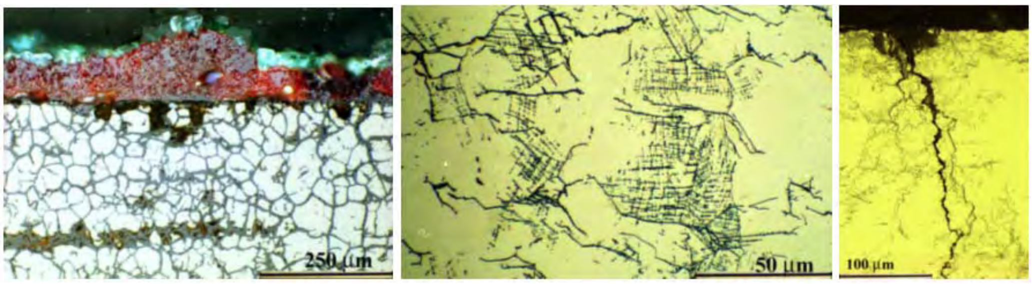


Fig.13 *Examples of selective inter-granular corrosion that preferentially attack grain boundaries and slip lines [21]*

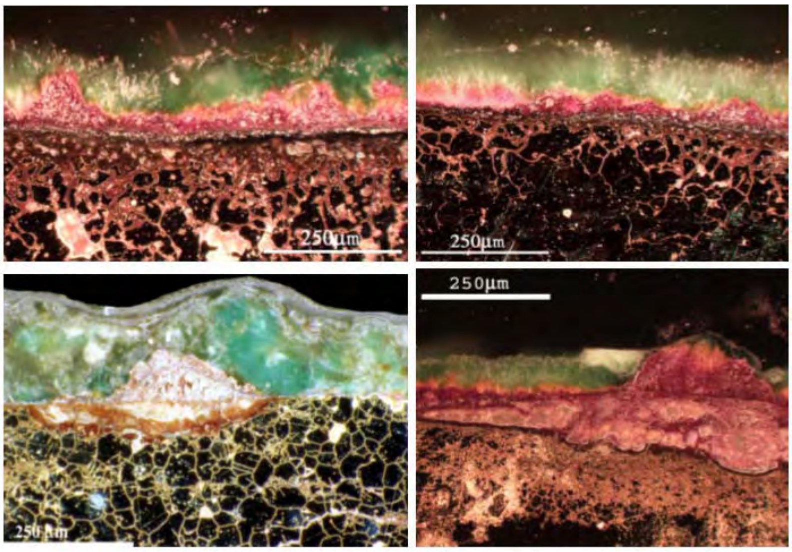


Fig.14 *Optical images for some selected Cu-base artefacts that disclose [21]*

- *the first stages of the bronze disease induced by the cyclic reaction between uncoated copper chlorides , oxygen and humidity (first raw);*
- *the presence of thick layer of cuprite or of Cu (II) compounds that protect the surface thus inhibiting the occurrence of the cyclic reaction.*

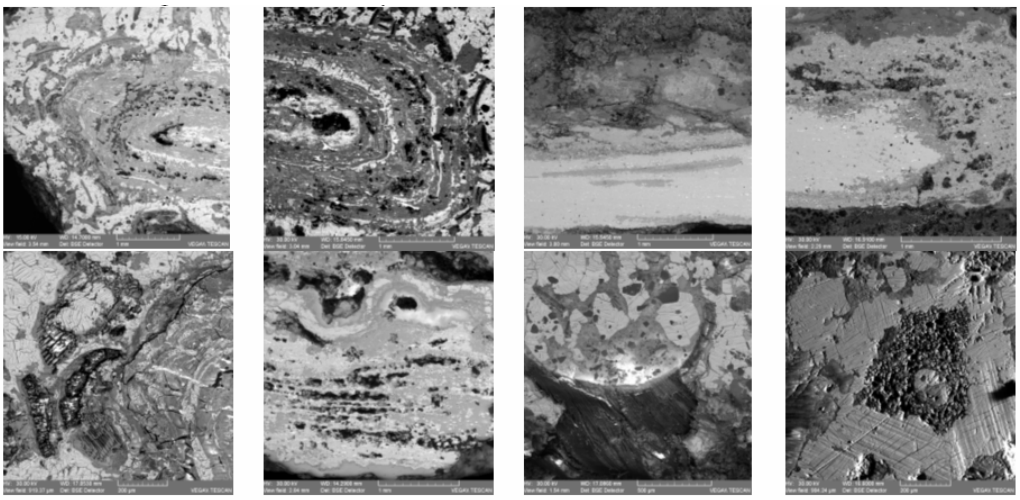


Fig. 15 *SEM images of some bronze coins (Xth Century) in cross-section: on first line is visible the Liesegang Effect in a non-disturbed archaeological site; on the second line are complex monolith structures with silicates, calionite, sulphides films, wood, micro-fossils.*

There also exist other effects such as:

- Diffusion and segregation effects, with the copper extraction and (the reduction of the copper concentration) or the reduction of the concentration in the active metals (see brasses) with the refining process (spongious structures)

- Fossilization and mineralization effects;

- Monolithasion effects and embedding effects of the mineral, vegetal or animal formations

- Effect of the lenses made up of lead, tin or other non-corroded metal in the case of the pieces with or without strongly brittled metallic cores, respectively

- Effect of the deep cracks which pass through the corrosion products up to both the metallic intercrystalline or transcrystalline cores (inter- or trans-granular) and the closed inner cracks, respectively

- Effect of the segregation of the compounds and their unidirectional crystallization.

4. Effects from Stress

Metallic pieces are subjected to the following stress groups:

- **Erosion Mechanical Stress** (EMS) – abrasion from the period when the object is used or from the archaeological site under the influence of the tectonic movements and groundwaters dynamics;
- **Stress Corrosion Cracking** (SCC), mechanism consists in the simultaneous action of a corrosive environment and mechanical load;
- **Corrosion and Irradiative Stress** (CIS) is due to the continuous corrosion of the environment and to the thermal or irradiative fluctuation from the environment;
- **Electrochemical and Erosion Stress** (EES), erosion and contact with metal of different chemical nature.

5. Conclusions

The paper, as a review, presents the different cases of the conservation state of the bronze artefacts. The multitudine and complexity of the cases reveal some problems in their classifying and in the establishing of the forming mechanisms of these corrosion products.

Thus, there has been established three main groups which determine the forming mechanisms of the corrosion products, namely, the environment aggresivity, the nature and the complex structure of the alloy, the obtaining alloy technology, the technology of the artefact manufacturing and the shape, the complexity and chemical reactivity of the corrosion products. As far as the corrosion products are concerned, a main role in the establishing of the forming mechanism of the archaeological patina is being played by the primary patina, especially by the products with high chemical inertia and with a protecting role by the surface passivation (e.g. phosphates, chalcokites, cuprites and silicates). Therefore, the protection role provided by the soils with phosphates and sulphides which form continuous passivant films.

This paper succeeds in rendering evident the role of these films in the accomplishing of the morphology and structure of the archaeological patina.

The forming of the secondary patina by the acid-base and hydrous processes above the primary patina (resulted from the redox processes) starts from the pre-abandon period and strongly goes on into the archaeological site under the influence of the pedological factors (chemical aggresivity, groundwater dynamics, soil tectonics, other physical and mechanical processes which perturb the archaeological site).

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