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THE USE OF MINERALOGICAL DATA IN INTERPRETATION OF BRASS ALLOY BRITTLENESS THROUGH A METALLIC OBJECT FROM MUSEUM OF FACULTY OF APPLIED ARTS IN CAIRO

Gharib ABEER*

Conservation department, Faculty of Fine Arts, Minia University, Minia 61519, Egypt

Abstract

Metallic objects undergo physical-chemical transformations involving complex mechanisms, which change both their surface and their metallic core. This paper presents the study of a Brass head of a princess from the museum of Faculty of Applied Arts in Cairo, in which we used Optical microscopy (OM), Metallographic microscope, Scanning electron microscopy, coupled with energy dispersive X- ray spectroscopy (SEM-EDX), and X- ray diffraction. The results revealed the excess of the chloride ion in corrosion products, transforming the bulk in stratified sponge structure. Compounds of primary and secondary patina were found as color stains on the surface. The alloy components (Cu, Sn, Zn) and contamination components, allowed us to prove the influence of environmental factors in the alteration processes of Brass alloy artifacts causing brittleness in the mineralogical composition. Finally, the results obtained helps in choosing the best methods of treatment and conservation.

Keywords: *Corrosion mechanism; Brass alloys Brittleness; OM; SEM-EDX; XRD.*

Introduction

The evolution of human culture and civilization has always excited both scholars and persons. Their main aim is to know the material and whether it suffered the effects of the implementation works of the discovery. They are also interested in the processes of elaboration and processing of material and of the implementation work and later interventions to restore the objects. In collaboration, the archaeologist and the scientific investigator can easily reach those objectives. Today we have modern systems of analysis, involving disciplinary techniques that allow an interdisciplinary, exhaustive interpretation [1].The studies performed on copper alloy objects a series of transformations, some major ones, which allow us to easily show their current state of conservation reached under exogenous or endogenous factors, with or without anthropic influences [2-3]. To study the evolution of underground degradation for copper alloy items, one should take into account both the crust and the metallic core, to determine characteristics, and certain compounds that formed during three periods: after manufacture until abandonment, after abandonment until burial, after burial once underground sinking started and the stay in certain stratigraphic layers until the discovery [4-5]. During the degradation mechanisms, copper alloy forms 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

* Corresponding author: abeer.ibrahim@mu.edu.eg

by passive action, and type II - formed after the 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 (cuprite Cu_2O, tenorite CuO) copper sulphides and sulfates (covelite CuS, chalcocite Cu_2S), hydrated copper carbonates (malachite $CuCO_3 \cdot Cu(OH)_2$), azurite $Cu_3CO_3(OH)_2$ and copper chlorides (nantokite $CuCl$, atacamite $Cu_2(OH)_3Cl$, paratacamite $Cu_2Cl(OH)_3$) are chemical compounds resulting from corrosion of copper [6]. Generally, the processes of chemical alteration resulted from the interaction between the artifact and its environment is composed from complexion reactions, assisted acid-basically, but also from a series of changes, with structural-crystalline reformations. In order to explain the degradation mechanism during the underground stay, one takes into account a series of factors: the chemical composition of the basic alloy and the manufacturing technology of the artifact, its state of conservation before abandonment, its age, the physical-chemical and microbiological characteristics of the soil, the depth where it was found, as well as the anthropic influences before and after abandonment [7-8]. A study of the corrosion features and the effects on archaeological objects is greatly important to clarify the corrosive media and the corrosion processes. Such kind of studies helps in selecting the conservation methods, which makes it significant for both corrosion science and archaeological objects. Many scientists used different analytic methods in this field, to investigate the morphology, structure and nature of the patina, or of the corrosion products on archaeological metallic objects. Those studies concentrated on finding a relationship between the surrounding environment, where they formed, and their micro-chemical structure [9-13].

Description a metallic head of a princess

The metallic portrait is exhibited at the museum of the faculty of applied arts in Cairo under no. 214/6. It is 6.8cm high (Fig. 1). The portrait perhaps represents Meritaten, the eldest daughter of Akhenaten new kingdom, 18th dynasty, 1365 - 1349 B.C. The portrait represents a happy blending of the mode introduced by Amenophis IV - elongated cranium and long, with the measured traits of the portrait of Nefertiti. The result is a work of the highest artistic quality whose softened expression has not lost any of its spiritual radiance (Fig. 1).

Fig. 1. Metallic head of a princess.

Methods

Microscopic investigations were carried out by using a Smart-Eye USB Digital Microscope at various magnifications between 100X and 200X, in order to characterize the morphological features of the corrosion products and to explore the nature of the patina.

A thorough examination and photography of the object performed with the metallographic microscope to show the structure of the object highlighted the degradation and deterioration of the object and processes that started at the burial time, due to different corrosion factors.*Scanning electron microscopy, coupled with energy dispersive X- ray spectroscopy (SEM-EDX) Analysis* Scanning electron microscopy (SEM) micrograph used to determine the morphology and composition of the alloy and the corrosion layers, model (EDAX AMMETER materials analysis division. Quanta FEG250 X1 Analyzer), The Quanta QX1 EDAX detector used for qualitative and quantitative microanalysis. The EDAX detector is the third generation, the X-Flash; that does not need liquid nitrogen cooling and is about 10 times faster than conventional detectors Si (Li). *X-ray diffraction analysis* The sample was tested by X-ray Diffraction (XRD) method on a diffractometer PHILIPS PW 1710 for powder, under the following conditions: operating voltage: U = 40kV, current I = 30mA, X-rays from a copper cathode (Cu), wavelength CuKα = 1.54178Å, graphite mono-chromator, test range: 4 - 90º 2θ, step: 0.02° 2θ, time constant: 0.5s (per step).

Results

Microscopic examination

Macroscopic observations allowed us to recognize the corrosion deposits and layers that completely cover object, color, nature, and shape. The characterization of the surface by Optical and Scanning Electron Microscopy (SEM) examinations was primarily carried out without any preparation to keep it intact [14]. Morphologically, the object has different corrosion crusts, in which we identified various microstructures, with fibers and soil deposits (Fig. 2), the globular button fragment characterized by a green corrosion crust, rough, inhomogeneous, with irregularities caused by the micro-structures from the soil (Fig. 3) and without uniform distributions.

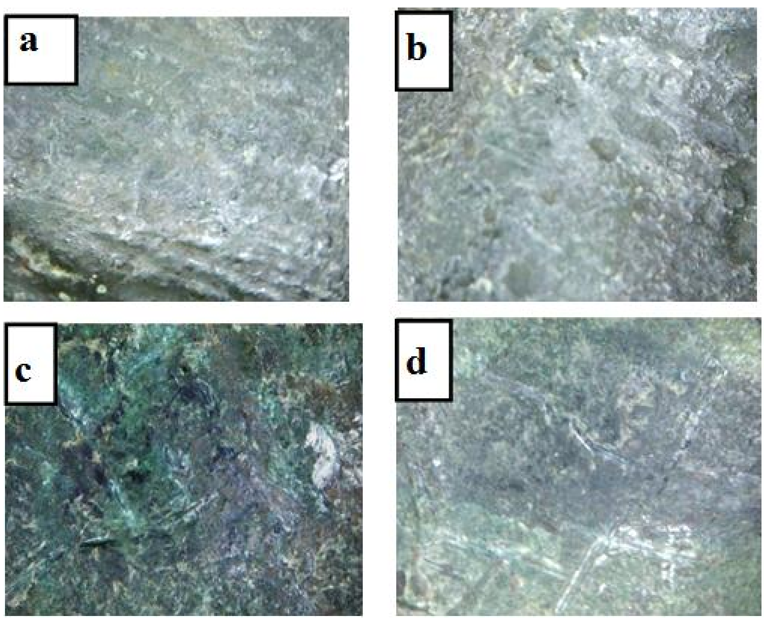

Fig. 2. Optical observation (50X): a - light green corrosion product, b - dispersed contamination microstructure, c - multicolor areas, d - mineralized fibers.

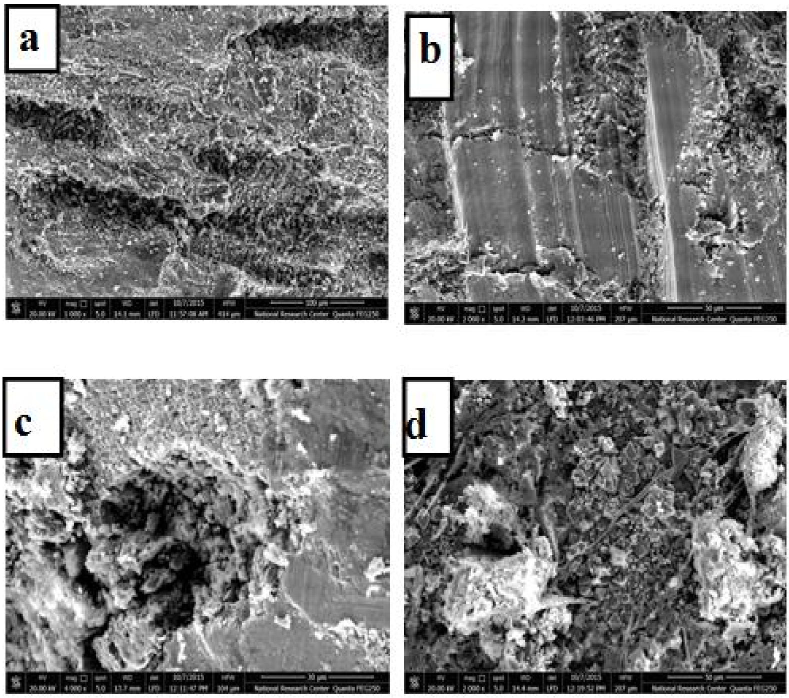

Fig. 3. SEM image of corrosion crust with different structure:
a - distorting of the structure1000X, b - cracks in the corrosion crust 2000X,
c - spongy structures 4000X, d - inter-granular corrosion 2000X.

Metallographic examination of a sample of the object showed crystals are irregular in shape, the boundaries along which they meet are rarely so, and most of the crystals that had some chance to adjust, the boundaries of a network which is quite similar to a froth of soap bubbles. The boundaries are smoothly curved, and they meet at 120 degrees because only at this angle are the surface-tension forces in local equilibrium. (Fig. 4) Shows crystal grains separated from a lump of beta brass. The nicely curved surfaces and the sharp edges where they meet will notice. The faces of these grains often elongation [15].

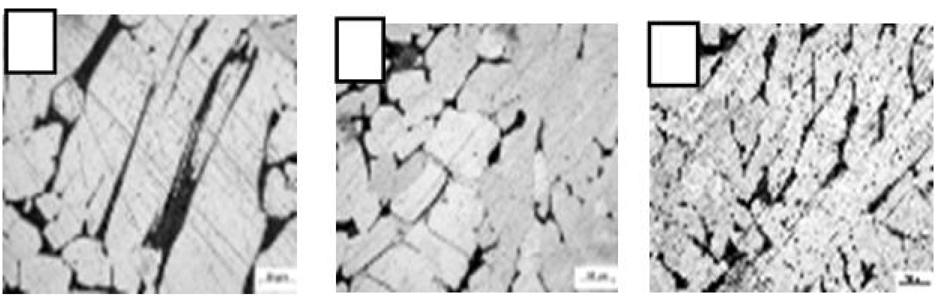

Fig. 4. Micrograph of samples (50X) Show elongation of grains.

SEM-EDX Analysis The EDX analysis revealed the components of the alloy (Cu, Sn and Zn) and contamination elements coming from the environment (S, O, C, Ca and Al) as shown in figure 5 and table 1.

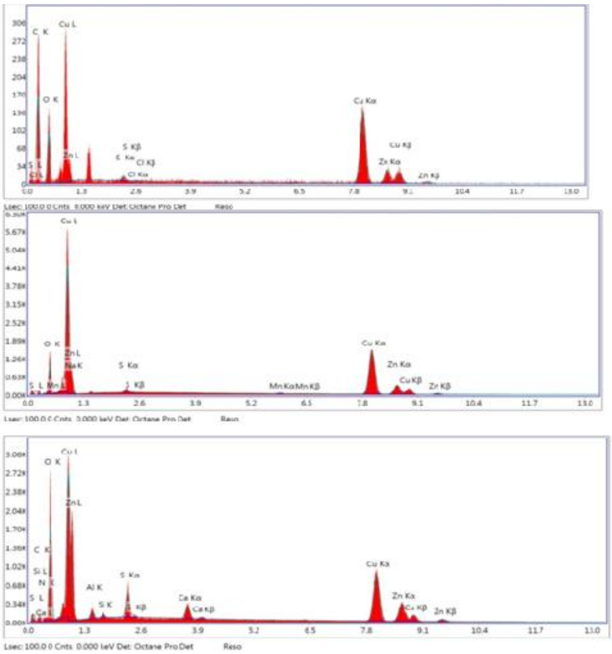

Fig. 5. EDX spectrums of samples show composition on surface and copper alloy.

Table 1 The EDX composition on surface and copper alloy.

Element	Weight%	Atomic%	Net Int.	Error%
C	**7.05**	**16.17**	**18.39**	**13.28**
N	**2.72**	**5.35**	**7.90**	**19.95**
O	**28.44**	**48.96**	**26.93**	**8.84**
Al	**1.27**	**1.30**	**23.64**	**14.44**
Si	**0.41**	**0.40**	**10.17**	**25.09**
S	**3.45**	**2.96**	**10.97**	**6.38**
Ca	**2.07**	**1.42**	**51.81**	**9.38**
Cu	**36.66**	**15.89**	**27.65**	**2.67**
Zn	**17.94**	**7.56**	**10.90**	**4.14**

X-ray diffraction analysis X-ray diffraction analysis showed that the dark green corrosion crust that covers the surface is Atacamite; and the corrosion compounds are Posanjakite, Cuprite, Copper, Tenorite, Quartz and Nantokite As shown in figure 6 and table 2.

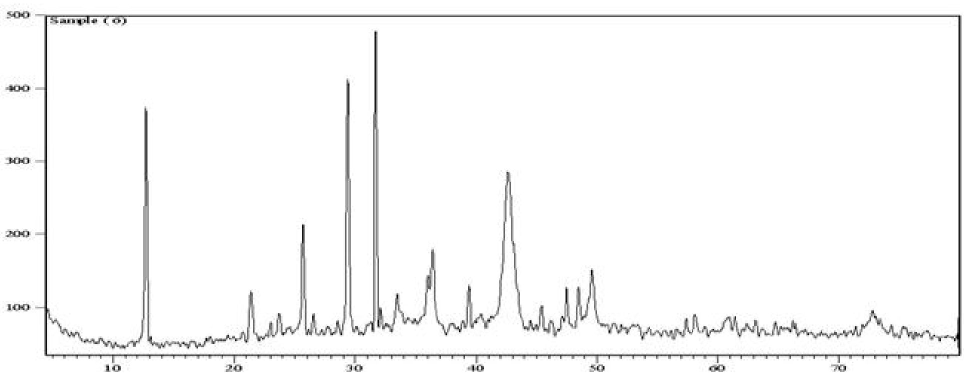

Fig. 6. X-Ray pattern representing the patina of the surface

Table 2. Mineralogical composition of corrosion products sample obtained by XRD

Minerals	Formula	Card No.	Content
Atacamite	$Cu_2(OH)_3Cl$	02-0146	Major
Posanjakite	$Cu_4SO_4(OH)_6.H_2O$	20-0364	Major
Cuprite	Cu_2O	05-0667	Traces
Copper	Cu	01-1241	Traces
Tenorite	CuO	05-0661	Traces
Quartz	SiO_2	33-1161	Traces
Nantokite	CuCl	06-0344	Traces

Treatments

Mechanical cleaning applied to remove the superficial deposits in a controlled and minimally obstructive way and then to reach a smooth layer which preserves the detail and shape. The cleaning procedure involved removing the soft, smooth corrosion and soil residues by mechanical means, such as by glass-bristle brushes, careful use scalpels and dental. To inhibit further corrosion after mechanical cleaning, the object were swabbed with acetone and inhibited with three coats 3% on Benzotriazole in ethanol by brush. One hour passed between each application in order to dry, coated afterwards with a protective coating of Paraloid B-44 5% in ethanol [16-19]. The coating was applied in 3 layers. In between each application the film was allowed to dry and polymerize for 8 hours. The appearance is showed in figure 7.

Fig.7. Metallic head of a princess after treatment and conservation.

Discussions

Microscopic observation by Optical and Scanning Electron Microscopy (SEM) examinations showed that physiochemical transformations occur during the lying time, which attributed to some deterioration processes (cracking, fragmentation, grinding or erosion) and chemical alteration (acid-basic and complexion reactions). The presence of stratified structures separated by micro-cavities is due to chloride ions in the buried area. Metallographic examination of a sample from the object showed that the object suffered from stress corrosion, term used to describe cracks in some metals as a result of common pressure for the mechanical fatigue and the corroded medium (union expansion pressure or internal tension and corrosion reactions), where some cracks created then spread in vertical direction of pressure. This occurs in alloys, which is exposed to changes in temperature and fatigues that occur for metal during its formulation, welding, thermal treatments or hammering process [20]. Surface analysis by SEM-EDX revealed a brass alloy (Cu, Zn and Sn). The contamination elements from environmental surrounding the object are due to chlorides, silicates, and sulfites ions. It is generally accepted that the surface layer consists of Cu (II) salts and salts of the sharing metals in the alloy. The resulted salts or corrosion products usually cover a red cuprous oxide layer (cuprite) that is next to the metal core. The corrosion products grew on the object were determined by X-ray diffraction analysis. Cuprite thin layer barrier is transformed to Nantokite; Nantokite detected as minor element in the sample, which generates other secondary patina compounds, which are soluble. Such contaminated structures deposited interspersed with secondary patina products as a layered sponge. Nantokite continuous oxidized to the powdery greenish patina of oxy-chloride as Atacamite [21]. Crystalline phase of Atacamite was the major element identified in the sample. The Atacamite appears to occur on the surface in two changes, first as thick sheets of corrosion, and secondly, as eruptions of Atacamite in the form of small pustules over this surface, which are covered with a thin layer of cuprite, which accounts for their brown/black appearance, as the thin skin of red culprit is underlain by the dark green of the Atacamite [22]. The green basic copper sulfate Posanjakite was found as a major compound in the sample, usually reported on artifacts exposed to sulfur-bearing waters or atmospheres.The secondary patina, developed in contact with some microstructures from the site, embeds them into the surface of the object (by processes of mineralization), forming the tertiary, or the contamination patina. The tertiary patina is shaped as a monolith bulk, with or without metallic core, with embedded microstructures of vegetal or animal fibers, insects, etc. Those microstructures of contamination from the site have a great importance in research, as they highlight some aspect evolution of the artifact [23, 24].

Conclusion

The study of a brass head of a princess, from different viewpoints is discussed in this paper, which showed that the non-uniform corrosion crust, with irregularities created by corrosion product, under the influence of Cl^-, HO^-, O^{2-}, and S^{2-} from the environmental surrounding the object, the corrosion compounds from the primary (Cuprite and Tenorite) and secondary patina (nantokite and etc.) are transformed into reforming structures from the tertiary patina (Atacamite and Posanjakite). Defects in processing and metal artifact brittle of the structure (cracks, scratches, debris from processing etc.) contribute to discontinuous crusts. Homogeneity/inhomogeneity corrosion products are related to the presence of microstructures embedded in the metal core in the archaeological site. Mechanical cleaning provides the only safe technique employed in the conservation of objects. It is easy, enables the conservator to have control over the cleaning process, provides greater familiarity with the object and ties in once more the principles of minimum intervention

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