Morphology, Technical and Treatment Study of Leaded Bronze, Applied On Some Archaeological Statues from Dhamar Museum, Yemen

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Abstract: ***A group of leaded bronze statues found during the archaeological excavation of Yemeni mission 2002 A.D, in Gabal al- lawd , Jawf area , Yemen and dated back to Minaean period in Yemen [sixth century B.C – 24 B.C], are now in the Dhamar regional museum. They suffered deterioration: three of these statues had a thick corrosion products of pale-green / black , the others had a rust-colored Black and Brown with the presence of small parts and scattered pale green. The aims of this paper are to study bronze alloy to get a deeper insight into the morphology and mineralogy of corrosion products. The cause and mechanism of corrosion process to control and stop it, and to identify the types of corrosion products of selected objects as well as their constituting metals in order to carry out scientific treatment and conservation to avoid any further deterioration. To achieve those specimens from the statues were examined by Metallographic Microscope (ME) and Scanning Electron Microscope (SEM), while the corrosion products were analyzed by X-ray diffraction (XRD). X-ray Fluorescence (XRF) was used to determine the bulk elements of the objects. XRD data showed that the corrosion products are cuprite, atacamite and paratacamite; whereas XRF analysis pointed out that the statues are composed by a leaded bronze alloy. Microscopic examination reveals that the statues suffered deterioration mainly in spots. Exploiting the collected info, chemical cleaning was chosen for treating the objects. Finally these obtained results helped us in treatment and conservation the selected objects.***

Keywords: Leaded bronze, Human statues, corrosion products, Morphology, Technical, ME examination, SEM, XRD, XRF, Treatment, Conservation

1. Introduction

Bronze was utilized extensively in ancient ages for making statues, vases, vessels, and weapons …..Etc. It was the preferred material for casting statues and other decorative artifacts because it reproduces every detail of the mold and because its high corrosion resistance ensures that the statue will last [1].The bronzes containing tin more than 10% are generally harder and more corrosion resistant than either of the pure metal. Addition of lead to bronze alloy was also known, as it improves the fluidity of the melted bronze alloy and thus makes it easier to machine. It has been reported that lead was added to bronze alloy in ancient Egypt during the Greek / Roman period until the percentage of it reached 32.5% in same statues and coins from that period, although it doesn't mix with the other contents of the alloy [2]. Egyptian dynastic art, small lost-wax bronze figurines were made in large numbers; several thousand of them have been conserved in museum collections. The ancient Chinese, from at least 1200B.C, knew both lost-wax casting and section mold casting, and in the Shang dynasty create d large ritual vessels covered with complex decoration which have survived in tombs [3].

The technology of high leaded bronze casting for producing mirrors was developed to a high level of sophistication in China during the late eastern Chou and Han periods (400-200 B.C). Romans also used these high Tin Cu-based alloys for producing mirrors whose chemical composition and structure were very similar to those used in China[4].Archaeologists have observed that on Chinese and Roman bronze mirrors these same areas are not corroded, and are still curiously characterized by a reflective and silvery-lustrous surface. The presences of these areas indicate that mirrors have successfully resisted corrosion for about two millennia and that the original finished surface is still present. Metal corrosion is a process of chemical dissolution. Cations migrate from the metal substrate and react with available anions to form the metal salts that constitute tarnish layers and corrosion crusts. The character and chemical makeup of the corrosion products depend on the nature of the substrate and the environment to which it is exposed[5].Most of the ancient bronze preserved in museums carry a green patina of basic salt, which is generally considered to add to their beauty. This patina may be described as protective as it prevented corrosion damage of ancient bronzes for a period of more than 2000 years [6]. During their burial; especially in desert dry sand or being exposed to non- polluted air out of doors. However occasionally in museums or in storage rooms , corrosion can occur if the objects are exposed to polluted atmosphere, moisture, chloride, or acid vapor. It has been reported that acetic acid coming from wooden boxes, where objects were stored caused serious corrosion to those objects [7].In fact not only acetic acid which coming from wooden boxes caused corrosion to the metallic objects, but also formic acid and others organic acids which coming from wood, wool, paper, and wall paintings, caused serious corrosion damage to the metallic objects in display or storage rooms. Extensive studies has been made on bronze disease, which is a dangerous cyclic copper corrosion phenomenon induced by exposure to aggressive environment, namely chloride and humidity, greenish color corrosion products of copper chloride is formed, which make cyclically reaction with the soil constituents, and the artifact that can disfigure the archaeological objects [8, 9, 10, 11].Sometimes, immersed or buried objects are covered with a biofilm. The microbiological consortia in the biofilms play an important role in determining the corrosion or alteration of such objects, particularly archaeological artifacts. Sulfating corrosion is a common consequence of bio fouling, because sulfur compounds are common in the biosphere and ubiquitous in the industrialized world. Sulfate-reducing bacteria (SRB), a diverse group of anaerobic bacteria isolated from a variety of sulfur-containing .The impact of sulfides on the corrosion of copper alloys has received considerable attention, including published reports documenting localized corrosion of copper alloys by SRB in estuarine environment[12].

Corrosion structures encountered in ancient bronze objects have many similarities to morphological processes that occur during the weathering of soils and rocks, yet the descriptive terms available, taken from metallic corrosion, are not adequate to describe the thick, complex mineral layers that are often observed on ancient bronzes [13].The information that can be derived from mineralogical study of ancient bronzes has a direct impact on the degree to which surface cleaning of such objects can be carried out during conservation.

This study aims to identify the ancient manufacturing processes, which were used to produce the statues, to get a deeper insight into the morphology and mineralogy of corrosion products. The cause and mechanism of corrosion process to control and stop it, and to identify the types of corrosion products of selected objects, as well as their constituting metals in order to carry out scientific treatment and conservation to avoid the further deterioration. This was achieved through a systematic study for six leaded bronze statues dating back to the Minaean period in Yemen [VI century BC - 24 B.C] and found during archaeological excavation in 2002 A. Din Gabal-al-lawd, Al-Gowf area.

2. Materials and Methods

2.1 Description and Condition

The dimensions of the statues are difference in size and scale. They suffered from the deterioration; the first three statues had a heavy crust of pale green corrosion products, incorporating soil particles, disfiguring them. The three others statues had a black and brown colored crust, with the presence of small parts and scattered pale green [Figs. 1, 2, 3].

They are classifieds the following:

1) The statue no. A, is a naked and a solid cast human statue with a strange face, its dimensions (6 cm length x 1.2 cm width). It suffered from deterioration factors, and covered with thick layers of the green/black corrosion products mixed with soil dirt (Fig. 1 A).
2) The statue no. B is a naked and a solid cast human statue with dimensions (6.5 cm length x 1.2 cm width). It suffered from deterioration factors, covered with thick layers of the green/black corrosion products mixed with soil dirt (Fig.1 B).
3) The statue no. C, is a naked and solid cast human statue, it has strange attributes with inconsistent and uncontrolled anatomical proportions. Its dimensions are (8 cm length x 1.2 cm width). It suffered from deterioration factors, covered with thick layers of the green/black corrosion products mixed with soil dirt (Fig.1 C).
4) The statue no. D is a naked and a solid cast human statue with dimensions (6.5 cm length x 1.2 cm width). It suffered from deterioration factors, covered with thick layers of the black corrosion (Fig.1 D).
5) The statue no. E is a naked and a solid cast human statue with dimensions (9.6 cm length x 1.2 cm width). It suffered from deterioration factors, covered with thick layers of the black corrosion (Fig.1 E).
6) The statue no. F is dressed and is a hollow cast human statue with dimensions (10.7 cm length x 2.3 cm width).It suffered from deterioration factors, covered with thick layers of the black corrosion (Fig.1 F).

A B C D E F

Figure 1: Statues before the treatment

A B C D E F

Figure 2: Statues before the treatment

Figure 3: Hollow statue [no. F] Before the treatment

2.2 Examinations and Analyses

The surface morphology of the statues was examined by metallographic microscope to determine the microstructure of the alloy and aspects of deterioration. Also a scanning electron microscope was used to more actually examination for the statues. X-Ray Florence analysis was used to determine the chemical composition of the statues, and X-Ray Diffraction analysis was used to investigate the corrosion products. It can provide valuable information related to the burial condition of the statues as well as the composition of the metal or the alloy [14].

2.2.1 Metallographic Microscope Examination (ME)

Metallographic examinations for samples of the statues were performed to show the microstructure of the metal and aspects of deterioration which spread on the metal surface [figs. no.4 - 9].

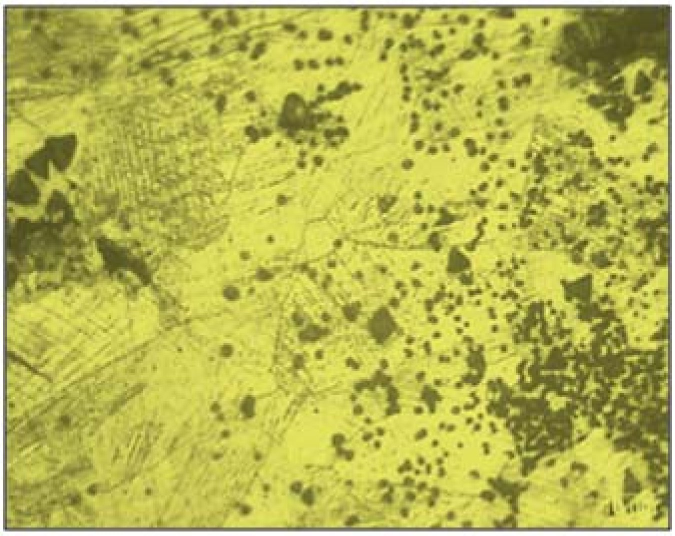

Figure 4: MEpho. for a sample from the statue No A shows the islands of lead in the alloy (50x)

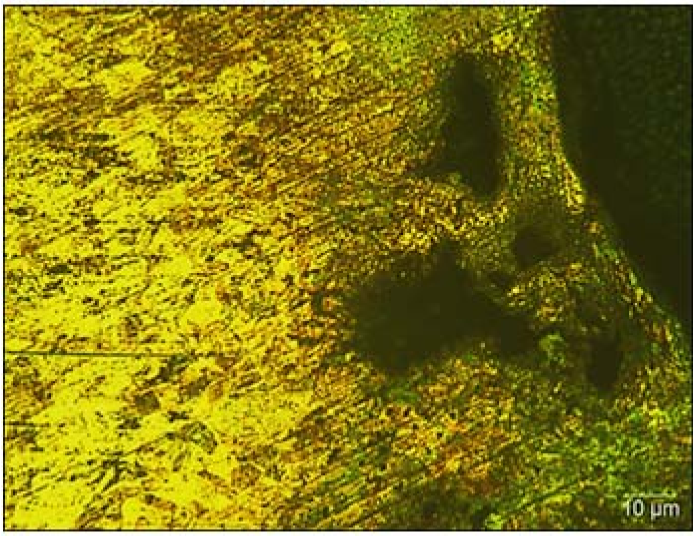

Figure 5: MEpho., for a sample from the statue no. B shows the pitting corrosion (50 xs)

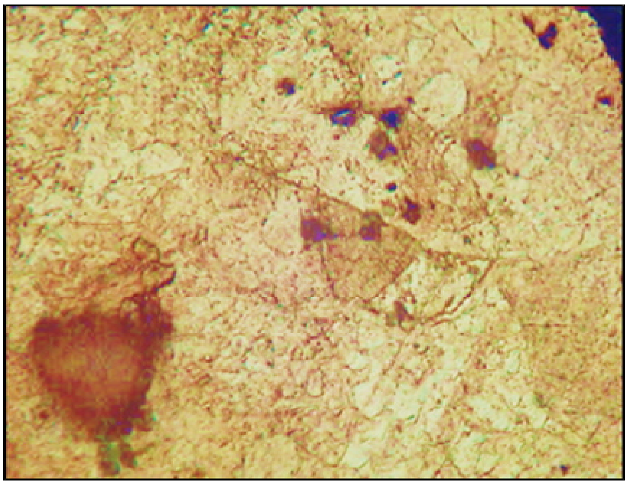

Figure 6: MEpho. for a sample from the statue no. C shows the micro crocks & blocks of lead (50 xs)

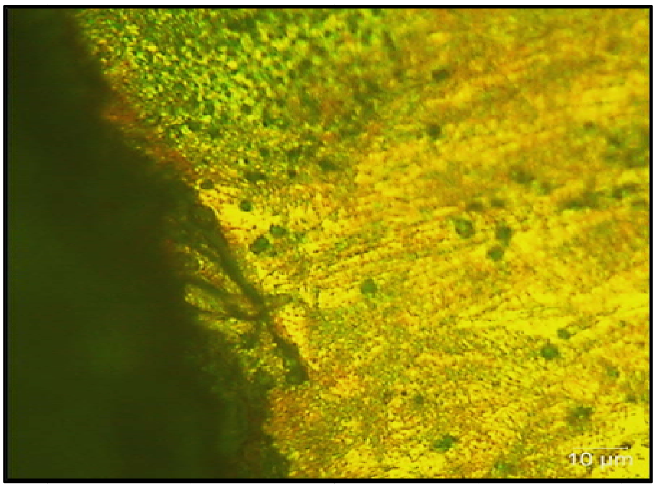

Figure 7: MEpho. for a sample from the statue no. D shows the Grieve corrosion & islands of lead in dispersed the alloy (50x)

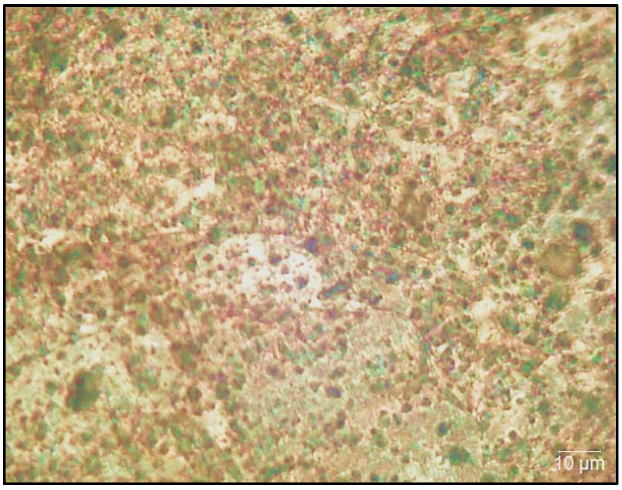

Figure 8: MEpho. for a sample from the statue no. E shows the blocks of lead dispersed in the alloy (50 xs)

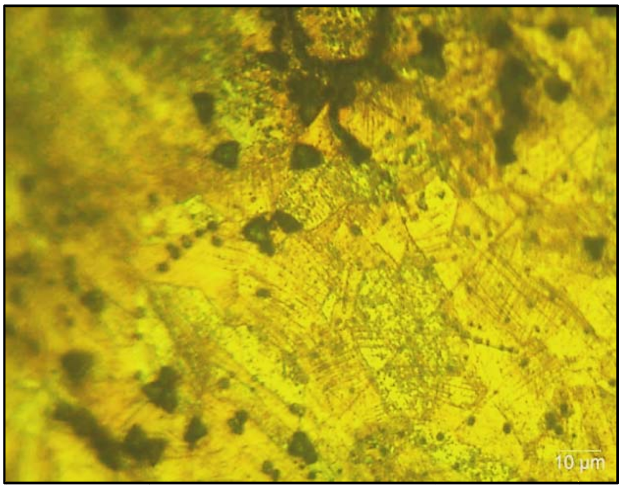

Figure 9: MEpho. for a sample from the statue no. F shows the islands of lead dispersed in the alloy (50x)

2.2.2 Scanning Electron Microscope Examination (SEM)

SEM examination of the statues showed the microstructure for the grains and aspects of deterioration; also a scanning electron microscope was used to more actually examination for the statues [figs. no. 10 – 13].

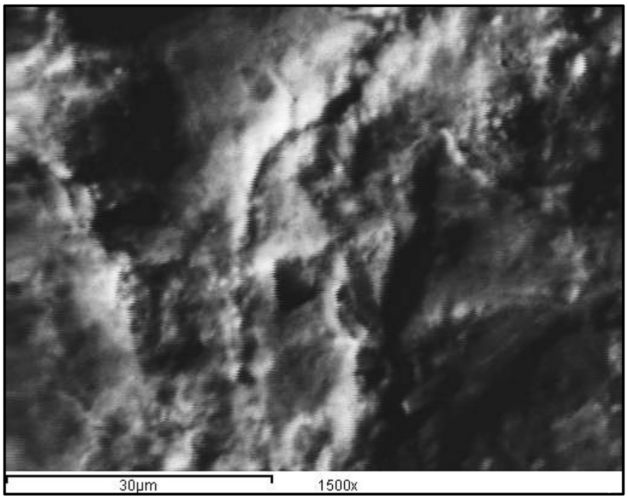

Figure 10: SEM photo for a sample from the statue no. A, suffers from micro cracks and distorting the surface (1500X)

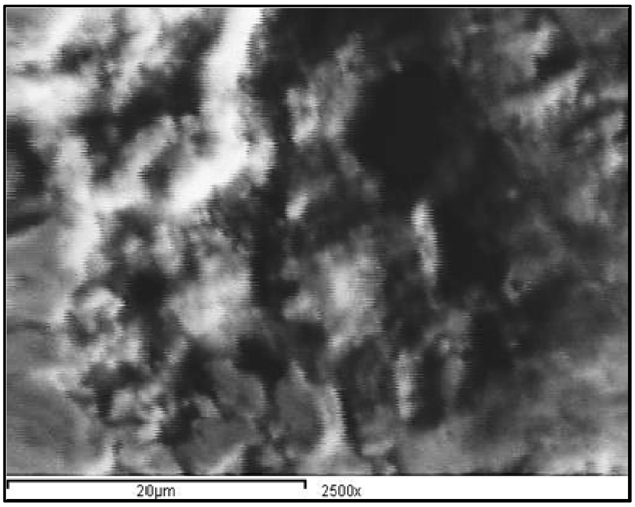

Figure 11: SEM photo for a sample from the statue no. B, suffers from pitting corrosion& distorting the surface (2500X)

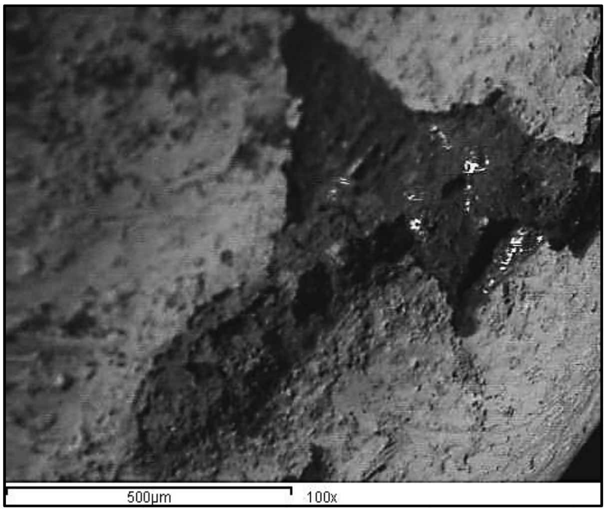

Figure 12: SEM photo for a sample from the statue no. C, shows a block of lead the alloy & pitting corrosion (100X)

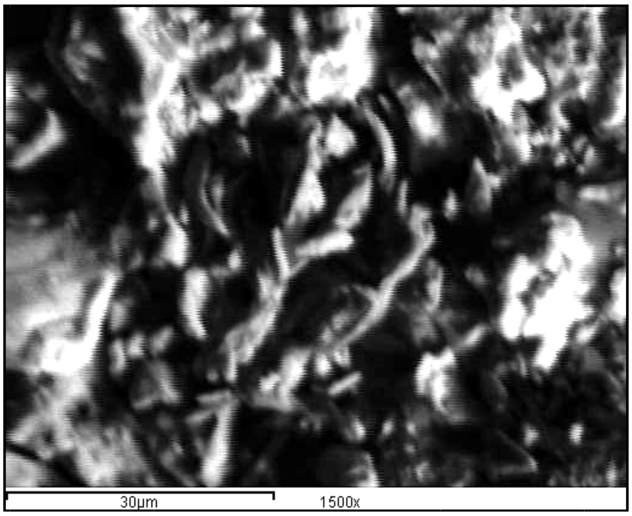

Figure 13: SEM photo for a sample from the statue no. F, suffers from pitting corrosion& distorting the surface (500X)

2.2.3 X-Ray Diffraction Analysis (XRD)

X-Ray diffraction analysis was carried out for corrosion product samples were taken from the surface of each object, by using A Philips X-Ray, Diffractometer type: pw1840 with Cu k& Radiation. The obtained diffraction scan given in figs. no. [14, 15, 16, 17] and the identified compounds represented in the table no. [1].

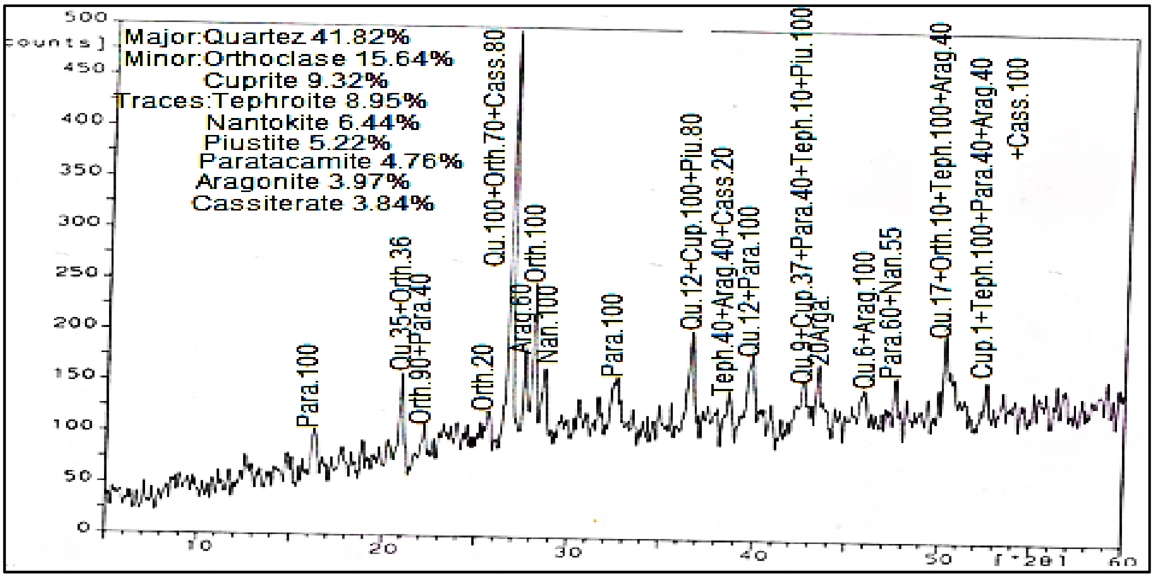

Figure 14: XRD pattern of corrosion products of the green patina statue no. A

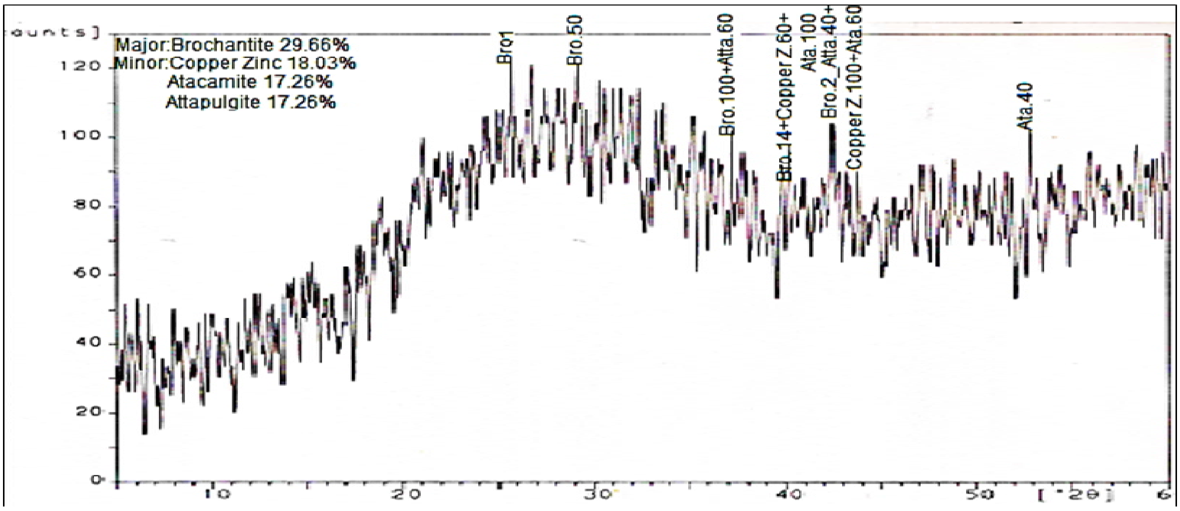

Figure 15: XRD pattern of corrosion products of the black patina statue no. D

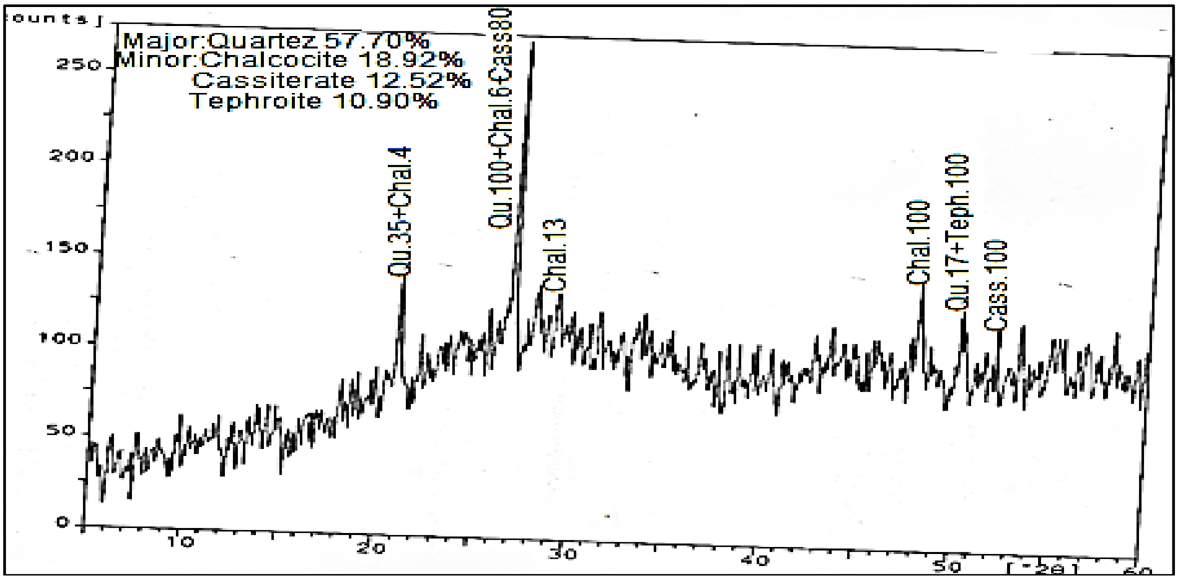

Figure 16: XRD pattern of corrosion products of the hollow statue no. F

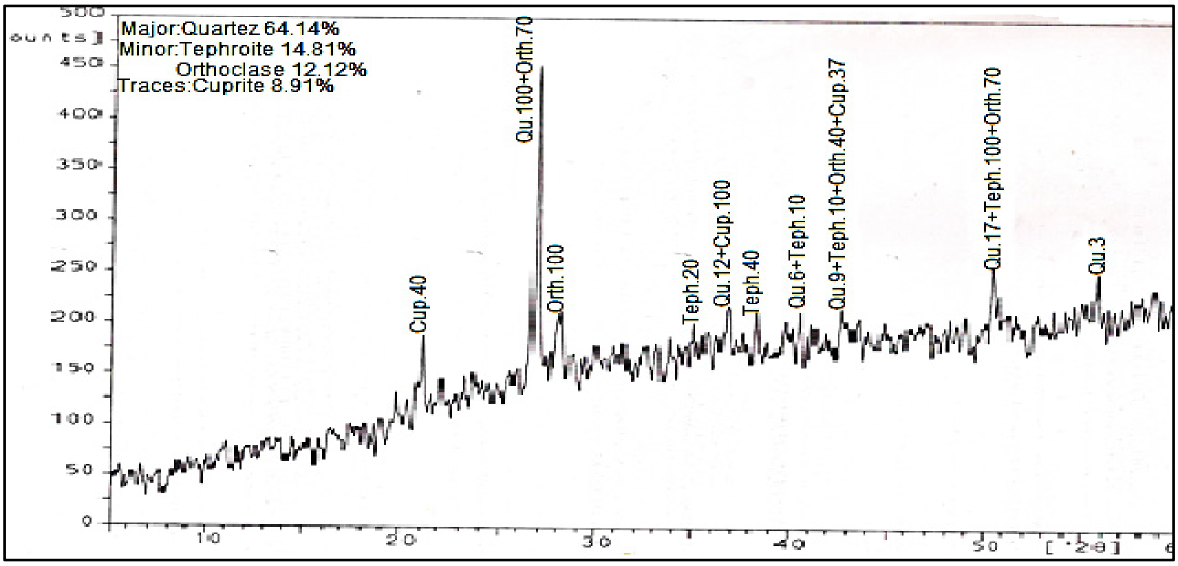

Figure 17: XRD pattern of the interior core (model) of the hollow statue no. F

Table 1: XRD analysis results of corrosion products of the Statues

Samples	*Compounds*		
	Major	*Minor*	*Traces*
The Statue No. A	Quartez SiO_2	Orthoclase$KAlSi_3O_8$ Cuprite Cu_2O	Tephroite Mn_2SiO_4 Nantokite Cu Cl Piustite Fe O Paratacamite$Cu_2(OH)_3Cl$ Aragonite $CaCO_3$ Cassiterate SnO_2
The Statue No. D	Brochantite$Cu_4SO_4(OH)_6$	Copper Zinc Cu Zn Atacamite$Cu_2(OH)_3Cl$ Attapulgite $MgAlSi_4O_{10}(OH)_{.4}H_2O$	
The Hollow Statue No .F	Quartez SiO_2	Chalcocite Cu_2S Cassiterate SnO2	Tephroite Mn_2SiO_4
The inner core of the hollow Statue No. F	Quartz Si O_2	Tephroite Mn_2SiO_4 Orthoclase$KAlSi_3O_8$	Cuprite Cu_2O

2.2.4 X-Ray Fluorescence Analysis(XRF)

XRF analysis of samples from the objects was performed to determine their composition by NITON/XL8138 (USA),driven with software version 4.2E. , as it is shown in the Table 2.

Table 2: X-R Fluorescence Analysis for the statues

Elements / *Samples*	*Cu%*	*S n%*	*P b%*	*Fe%*	*Zn%*	*Total %*
The statue no. A	58.36	11.56	29.03	0.15	-	100
The statue no. B	60.14	12.60	26.23	1.03	-	100
The statue no. C	59.43	11.89	27.10	1.35	0.05	100
The statue no. D	57.20	13.61	28.11	0.80	0.74	100
The statue no. E	60.21	12.10	25.30	0.3	12.08	100
The statue no. F	56.31	13.94	29.10	0.65	-	100

3. Treatment and Conservation of the Statues

According to the obtained examination, the statues have a good metallic state, but they are covered with thick layers of corrosion products. Chemical treatment was chosen-assisted by skilled mechanical cleaning. This helped us to reveal and discover the original surface topography.

The treatment procedures included the following steps:

1) Soaking the objects completely in solution of alkaline Rochelle salt (50 g m/L of Sodium hydroxide + 150 g m/L Sodium potassium tartrate) that was changed many times assisted by gentle mechanical cleaning with silk brush from time to time to dissolve the corrosion layers of copper [II] compounds. This step succeeded in removing green copper corrosion products and left a red/black layer covering the surfaces.
2) To dissolve and remove the oxides layer [Cuprite Cu_2O and Tenorite Cu O], 3% solution of sulphuric acid was used assisted by a brush to remove the loosed layer. This was done with regular checks and removing loosened layer, these procedures succeeded in removing all the corrosion products.
3) After that the statues were soaked in water and washed by a tooth brush to dislodge residue from crevices.
4) Repeated washing in hot deionized water bathes with altering heating and cooling, to ensure flushing capillaries to remove any chemical residues.
5) Drying in repeated bathes of ether and ethanol, followed by drying in hot sawdust, and mopped dry with soft clean cloth.
6) Finally the statues were isolated with paraloid B-72 dissolved in acetone 3% by using a brush Figs no. [18, 19, 20, 21, 22].

A B C D E F

Figure 18: Statues after treatment and conservation

A B C D E F

Figure 19: Statues after treatment and conservation

A B C A B C

Figure 20: Statues no. [A ,B ,C]after treatment and conservation

D E F D E F

Figure 21: Statues no. [D ,E ,F]after treatment and conservation

Figure 22: Hollow statue no. [F]after treatment and conservation

4. Results and Discussion

By studying the structure and constitution of the grains and phases of these statues, an understanding not only of the properties of a particular metal but also the history of its manufacture may result. For instance, the metallographic investigation serves in revealing the nature of ancient technology of the objects. The ancient manufacturer used the lost-wax casting process [Solid cast and Hollow cast techniques] to manufacture the statues. Also the study distinguished one alloy for the selected statues, they were made of a ternary alloy [copper/tin/lead]. The percentage of Tin varied from 11.56 % to 13.94% and the percentage of Lead varied from 25.30 % to 29.10.

The investigation results indicated that the majority of the investigated statues were made of leaded bronze and that the lead content varied from about 25.30 % to 29.10 %, and also a high amount of Tin ranged from 11.56% to 13.94%. Tylecate [15] mentioned that the cost of Pb bronze alloy is low with respect to more expensive and rarer Tin; therefore, the use of Pb bronze is justified from an economic point of view. But in the current study the examination and analysis of the selected statues indicated that the statues had a high amount of Lead and Tin.

The study showed that the ancient Yemeni manufacturer knew lost-wax casting, [solid cast, and hollow cast] to manufacture the statues. In solid cast, the manufacturer was started by making a full-sized model of the statue using wax and make all the details in it, then covering the wax model with clay to make the exterior mold and making two holes, one in the top and the other to the bottom of the clay mold , then the mold was left to dry and heated in a kiln until it transfers to a fired mold and the wax runs out through the holes and leaves the fired mold contents. The figures and details of the statue stamping inside it. After that the manufacturer closed the bottom hole and filled the liquid metal or alloy from the top hole, when the metal has cooled, the external mold was chipped away, revealing the metallic statue. Finally the manufacturer polishes it, shows the features and makes the fine details.

For hollow statues, a core is made of clay mixed with glue to make model for the statue, then covering it with the liquid wax and when the wax cooled, the manufacturer makes the small details in it. The complete wax structure is then invested in another kind of clay mold; the manufacturer covered the wax with the clay to make the exterior mold, and making the two holes in top and bottom of the mold where gases could be trapped and fill the liquid metal. Also the manufacturer used to put numbers of long metal nails a cross the group. When the exterior mold was dried, it was heated in a kiln until the clay mold transfers to a fired mold, and the wax runs out. The interior model has been already fixed by the metallic nails which were crossed through the group. Then, the manufacturer closed the bottom hole and the investment is then soon filled with liquid metal, or alloy through the top hole. After the metal has cooled, the external mold was chipped away, revealing an image of the wax form. The interior core material was removed to reduce the likelihood of interior corrosion, but sometimes the interior core material wasn't removed, and stays inside the statue forever. As it is shown in the figures of the hollow statue no. F. The exterior parts of nails were removed with a saw and polished away. Also incomplete voids created by gas pockets, or investment inclusions are then corrected. Small defects where vents were attached are filled and polished. This technique was used with the big statues to avoid consuming a large amount, of the alloy, and to avoid the heavy weight of the statue.

This study has produced new insights concerning the identification of component materials of the leaded bronze artifacts characteristic of ancient Yemeni metallic objects. The addition of lead to bronze alloy has many advantages in spite of the fact that it decreases the bronze mechanical properties as well as the fear of enhanced selected corrosion or galvanic corrosion. Leaded bronze alloy doesn't have interior corrosion resistance than normal bronze alloy, when exposed to moist air or mild soil, as the presence of lead will produce protective coating or insulating coating.

The results of the metallographic examination indicated a non-homogenous structure, localized corrosion spots and the existence of lead islands in the alloy. and aspects of deterioration, SEM results confirm metallographic examination results. In spite of this condition, the Galvanic corrosion tendency when the alloy is exposed to moist air or soil isn’t possible as lead compound is electrically insulating.

When Cu-based alloys are exposed to polluted atmosphere or to soil containing aggressive ions, greenish colored corrosion products are mainly formed on the surface. It is commonly known as patina , it was usually composed mainly of cuprite as the first layer formed on the surface of the objects, and basic copper chloride [Atacamite , Paratacamite….etc.] , depending on the content of environment [water , chlorides , sulfates , carbonates , ammonia…..etc.]. Corrosion process can take a long time as happened on copper base artifacts .The constant presence of chloride in the soil is responsible for the so-called [bronze disease]. Furthermore, the bulk alloy structure of these bronze statues clearly indicates the presence of as cast dendritic structures that can be preferentially attacked by aggressive agents.

XRD analysis results declared that the corrosion products of the statues essentially composed of Cuprite Cu_2O for all the group , in addition to other compounds such as Atacamite, Paratacamite, Brochantite, Chalcocite, Quartez , Orthoclase and Cassiterite. The formation of chlorides and sulfates resulted from the interaction between surrounding environment and the statues. The impact of sulfides on the corrosion of copper alloys has received considerable attention, including published reports documenting localized corrosion of copper alloys by Sulfate-reducing bacteria (SRB). A diverse group of anaerobic bacteria isolated from a variety of sulfur-containing a porous layer of cuprous sulfide with the general stoichiometry forms in the presence of sulfide ions . Copper ions migrate through the layer, react with more sulfide, and produce a thick, black scale, which can be altered by oxygen from the environment to a complex sulfide-oxide scale. The sulfide scale does not confer much protection against further attack, but the sulfide-oxide scale provides even less. Corrosion products on copper alloys were more adherent and in some cases difficult to scrape from the surface. In all cases, bacteria were closely associated with sulfur-rich deposits. There is one class of conditions under which biofilms appear not to produce sulfide minerals. If conditions at the surface of a copper alloy permit precipitation of nantokite (CuCl) under the cuprite layer, the alloy becomes vulnerable to bronze disease or pitting corrosion, depending on mass transport conditions. The presence of alloying elements does not protect against the formation of nantokite and the consequent bronze disease corrosion, though it probably affects the kinetics. The role of biofilms in the forms of corrosion associated with nantokite is not well understood, though biofilms are frequently observed and acid-producing bacteria could help produce the requisite conditions by increasing acidity in anodic regions, and restricting cation transport away from the surface, maintaining higher copper ion concentrations. Bronze disease and sulfiding microbiologically influenced corrosion are not observed in the same region, perhaps because the local redox environment required to produce bronze disease is too oxidizing for sulfiding. Another possibility is that the copper ion concentrations associated with nantokite, malachite, and the various polytypes of $Cu_2(OH)_3Cl$ may make the local environment toxic for SRB.

5. Conclusion

- The study indicated that leaded bronze alloy was used to make statues in ancient Yemen .
- Results showed the morphology of the surfaces and the elemental compositions of the corrosion products depend strongly on the chemical composition of the alloys.
- It is necessary to consider the soil micromorphology in order to determine the evolutions of the soil characteristics such as decalcification, modification of buffering capacity.
- The materials investigation is an necessary step in the documentation of the properties of the components materials of on object, it can help us in solving, interpreting many problems, also help us in choosing the best methods of treatment and conservation.
- Corrosion products associated with artifacts can provide information about original composition, and the environment in which they were preserved.
- It seems that Pb bronze alloy was used extensively in various other applications than coins or statues. Therefore, more studies are needed to carry out systematic non-destructive characterization of ancient leaded bronze artifacts.
- Unlike warty corrosion associated with chloride ions, the kind of warts seen on the surface of these bronzes are chemically stable formations. Under proper storage-or exhibition conditions and do not require especially strict humidity control in display or storage.

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