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A COMPARATIVE CHARACTERIZATION AND PRACTICAL STUDY OF BRONZE PATINAS AND CORROSION MECHANISM, APPLIED ON SOME ANCIENT OBJECTS FROM EGYPT AND YEMEN

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Abstract

A large number of studies on ancient bronze have tried to establish the chemical characteristics and structure of natural patinas grown up artifacts exposed to soil or the ambient atmosphere for a long time, these archaeological artifacts represent excellent samples for such studies, since the laboratory experiments have been carried out for a short time. The aim of the present paper is to study bronze alloy to get a deeper in sight into the physical and chemical characteristic of its patinas, the causes 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 for preservation to avoid the further deterioration. To achieve this purpose, a group of bronze objects from Egypt and Yemen have been selected for investigation of their chemical composition, metallurgical features and corrosion products, analytical and characterization study on areal bronze samples was performed, using Metallographic Microscope, Scanning Electron Microscope, X-ray Diffraction Analysis, and X-ray Florence Analysis. Also a systematic approach was used while practicing on a group of archaeological bronze objects from different areas in Egypt and Yemen, the two studies were connected and compared. Exploiting the collected info, chemical cleaning and electrical reduction methods were chosen for treating the objects.

Keywords: *Bronze; Patinas; Corrosion mechanism; Metallographic examinations; SEM, XRD and XRF analysis; Conservation state*

Introduction

The metals are not particularly stable and in most natural environments, they tend to react with other components to form more stable compounds. Galvanic corrosion may arise when two dissimilar metals are in contact and in an aqueous environment; the potential difference between them will initiate attack on the less noble of the two metals at a corrosion rate, which is largely dependent upon the surface reactions of the two metals [1].

Oxygen is more concentrated at one point of the surface than it is at another; this area will assume the role of the cathode, whilst the low oxygen in areas will corrode [2]. This is called a differential aeration cell and can be seen when area of metal under a rivet corrodes at the expense of surrounded metal [3, 4].

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High energy areas are inclined to lose electrons more readily than low–energy areas since there is high energy where one crystal lattice meets another, grain boundaries within a metal will become anodic to the enclosed gain and will corrode preferentially [5].

The difference of potentials can be found in junction metals either mechanically by folding, riveting or by soldering using heat [6], in addition to the difference in working techniques and heating treatments.

Extensive studies on ancient and historical bronzes have tried to establish the chemical characteristics and structure of natural patinas grown on the artifacts exposed for long time in soil, atmosphere, water or sea water [7-14]. Different surface patterns have then been observed, depending on the corrosive environment (chemical composition, pH, resistivity, etc.), but also on other non-negligible parameters such as historical periods, metallurgical techniques or even kind and size of artifacts [15]. The corrosion deposits are often complex, stratification of structure layers, inter-granular or trans-granular corrosion, etc., hove been pointed out [16, 17]. Also studying large numbers of individual artifacts of all kinds, not related to archaeological contexts or to the intrinsic metallurgical or chemical features of the artifacts [18, 19]. Furthermore, most of the published studies have also been carried out in view of improving preservation procedures, in order to prevent the so-called bronze disease a post burial cyclic corrosion phenomenon occurring in the atmosphere [20], due to the presence of cuprous chloride within the patinas-rather than to get a deeper insight into the corrosion behavior of Cu-Sn alloys in natural environments, despite the fact that some authors have attempted to describe the corrosion processes, very little yet known about the actual nature of patinas and about the processes governing the formation of the corroded structures.

So to avoid the previous shortage, some archaeological bronze objects have been selected as representative of different areas in Egypt and Yemen have been studied by systemically using the same methodological approach and analytical techniques using ME (metallographic examinations), SEM, XRD, XRF.

This work is structured around three approaches:

a. Characterization of the corrosion products layers, before, during and after treatment is made by morphological, elemental and structural analyses by complementary characterization techniques at various scales.

b. In order to more accurately understand the corrosion products is companied by a serial of investigation and analysis. It was done in two directions, the first direction working on corrosion systems coming from archaeological samples, these samples from archaeological objects from different areas in Egypt and Yemen, also to high light the reactivity phenomena, the second direction working on the sites of excavations by analysis samples from the soil, where is the objects were excavated in order to know its role in the corrosion process.

c. A more in depth structural study of corrosion products is planned to determine the causes and it is controlled.

Materials and Methods

Description and Condition

The investigations were conducted on a collection of archaeological objects from different environments in Egypt and Yemen, as the following:

- A statue of God made of bronze with dimensions: 12cm(length) x 3.7cm(width), it was discovered in excavation of Tell-Habua 1, North Sinai, Egypt, season 2004, by the Supreme Council of Antiquates mission and it dates back to 18th dynasty, Pharaonic period (1750 – 1309 B.C), it suffered from deterioration factors and aspects such as existing a thick and crusted layer of the green corrosion products mixed with soil dirt's and separated into two parts (Fig. 1a).

- Three statues of Gods, they were discovered in excavation of Tell-Habua 2, North Sinai, Egypt, season 2005, by the Supreme Council of Antiquates mission and they date back to 18th dynasty, Pharaonic period (1750 – 1309 B.C). They suffered from deterioration aspects, covered with a thick layer of the green corrosion products mixed with soil dirt's (Fig. 2).
- A dagger with dimensions: 20cm (length) x 4.7cm(width) x 1.3mm(thickness), it was discovered in excavation of Tell Atreib, Benha, Egypt, season 2007, by the Supreme Council of Antiquates mission, it dates back to Pharaonic period, New kingdom (1750-1080 B.C). It had a thick layer of green corrosion products, suffered from a partial mineralization and separated into two parts (Fig. 1c).
- A statue of Camel made of leaded bronze and manufactured by hollow casting technique with dimensions: 6cm(length) x 8.3cm(height), it was discovered in Gabal Al-laud site, Al-Gouf area, Yemen, season 2002, it dates back to Minaean period (6th century to 24 B.C) and now it is preserved in Dhamar regional museum, Yemen. It suffered from deterioration factors and aspects such as existing a thick and crusted layer of the green corrosion products, a partial mineralization and it lost its behind two legs (Fig. 3).
- Three bracelets in different dimensions (the circular of the first one 5cm and the two others 4cm), they were discovered in Harran site, Dhamar, Yemen, season 2003 and date back to Himyarite period (1000 B.C), the bracelets suffered from weakness and had a thick layer of corrosion products mixed with particles of soil (Fig. 4).
- An imprinting with dimensions (3cmx2.2cm), it was discovered in El-Shab El-Aswad site, Jahran district, Dhamar, Yemen, season 2006. They date back to Qatabanian period (1500 B.C), they had a thin black layer of corrosion products (Fig. 5).

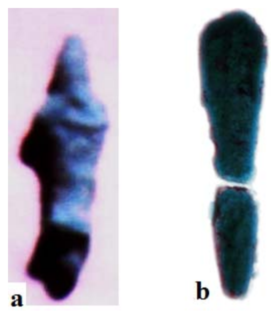

Fig. 1. The images of the bulks found in archaeological site:
a – the statue, b – the dagger.

Fig. 2. The three Gods statues before the treatment (Egypt)

Fig. 3. The statue of Camel before treatment (Yemen)

Fig. 4. The three bracelets before treatment (Yemen)

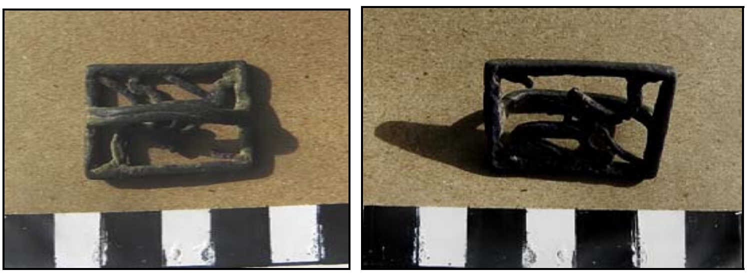

Fig. 5. The imprinting before treatment (Yemen)

Examinations and Analyses

Metallographic and Scanning Electron Microscope examination were used to study the surfaces morphology and microstructure of the objects, corrosion products were analyzed by X-Ray Diffraction method and X-ray Florescence was used to identify the chemical composition of the selected objects.

Metallographic Microscope examination (ME)

Metallographic examinations for samples of the objects were performed as the following:

- The God statue shows the microstructure of the metal and the corrosion along the grain boundaries (Fig. 6a).
- The Gods statues shows the microstructure of the metal and the pitting corrosion which disperses on the metal surface (Fig. 6b).
- The dagger show a partial mineralization of the metal, but also shows the existence of a sound metallic core (Fig. 6c). Figure 6d shows ME for another sample of the dagger after the successful treatment by electrical reduction method.

- The Camel statue shows the contents of Leaded bronze alloy and the existence of Lead islands disperses in the alloy (Fig. 6e).
- The bracelets shows the pitting corrosion and micro cracks spreads on the surface (Fig. 6f).
- The imprinting shows the contents of the alloy in distinguished colors and the Crevice corrosion which spreads on the edge of the metal (Fig. 6g).

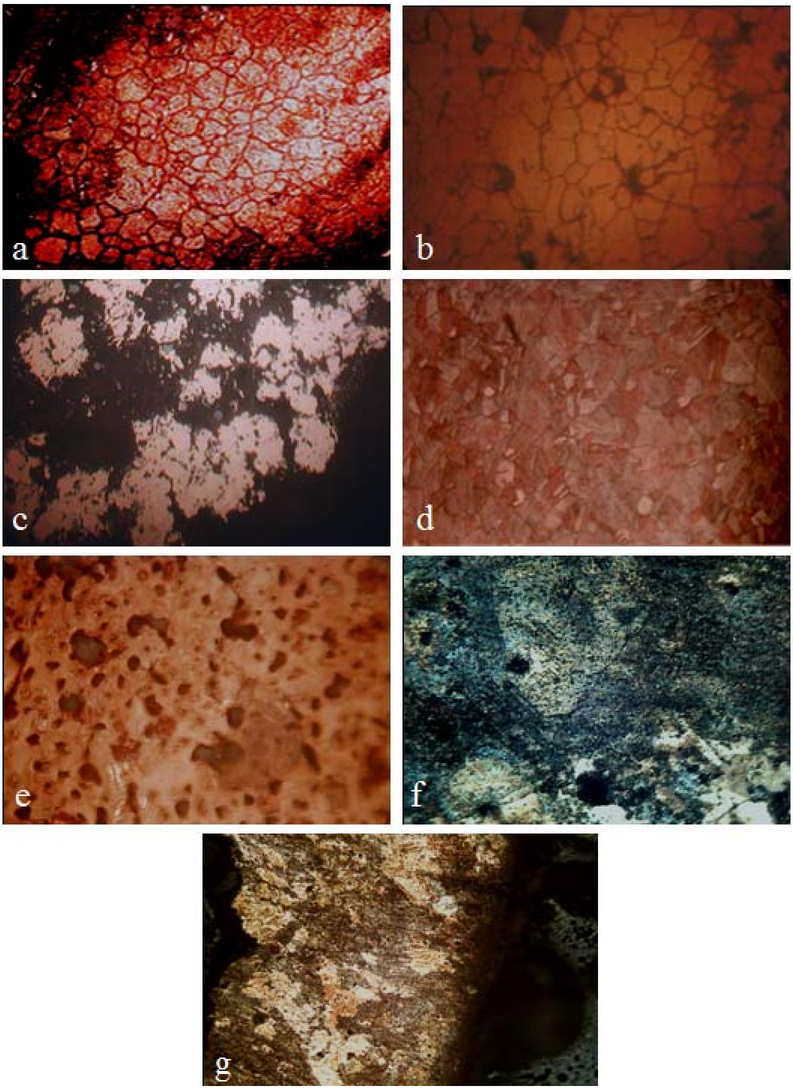

Fig. 6. Microphotography by ME of surfaces: a – The God statue (150X), b – The Gods statues (150X), c – The dagger before treatment (225X), d – The dagger after treatment (225X), e – The Camel statue (150X), f – The bracelets (150X), g – The imprinting (150X)

Scanning Electron Microscope examination (SEM)

SEM examinations for samples of the objects were performed as the following:

- The God statue shows the microstructure of the grains and the Crevice corrosion disperses on the grain boundaries (Fig. 7a).

- The Gods statues shows the pitting corrosion disperses on the surface, it confirms the obtained result by ME (Fig. 7b).
- The dagger shows the partial mineralization of the metal, but the core is still in a metallic case (Fig. 7c). Figure 7d shows SEM examination for a sample from the dagger after a successful treatment by electrical reduction method.
- SEM examination for a sample of the Camel statue shows the pitting corrosion which disperses on themetal surface (Fig. 7e).
- The bracelets shows the pitting corrosion spreads on the surface, that confirms the obtained result by ME (Fig. 7f).
- The imprinting shows the Crevice corrosion which disperses on the metal surface (Fig. 7g).

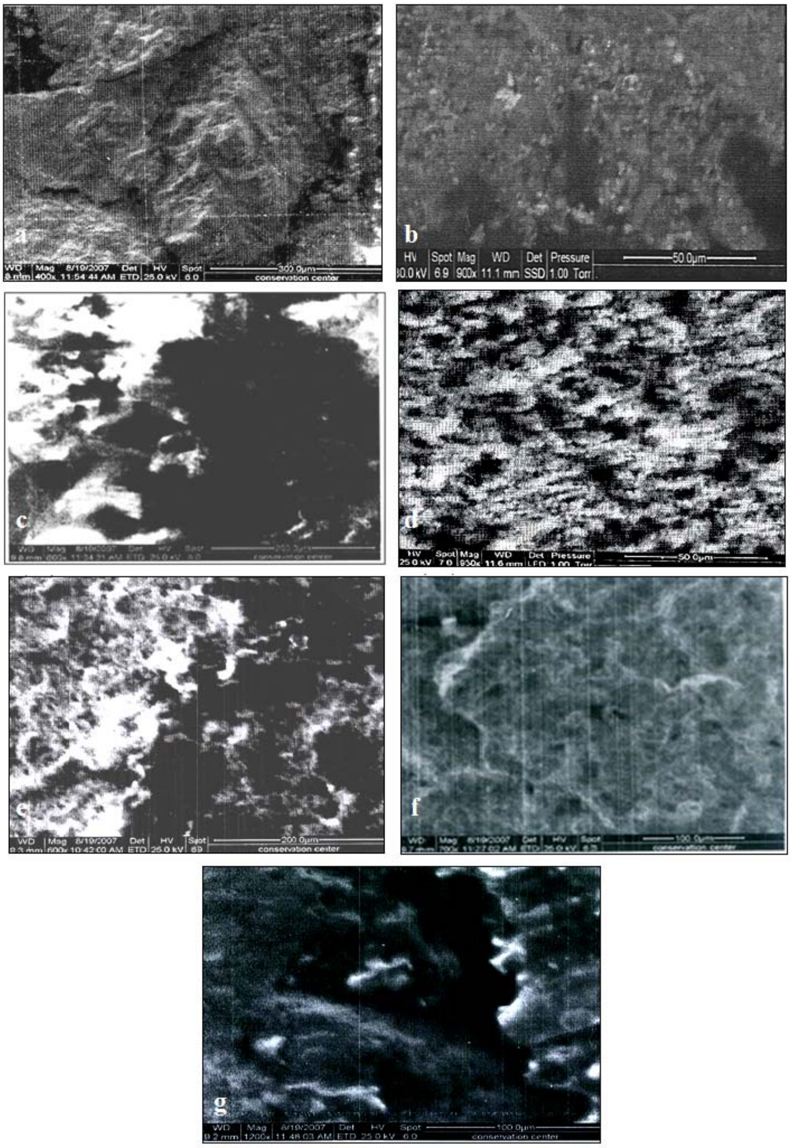

Fig. 7. SEM images of the sample surfaces: a – The God statue (400X), b – The Gods statues (900X), c – The dagger before treatment (600X), d – The dagger after treatment (950X), e – The Camel statue (600X), f – The bracelets (900X), g – The imprinting (1200X)

X-ray Diffraction (XRD) Analysis

X-ray diffraction analysis was carried out for corrosion product samples were taken from the surface of the objects and from the soil where these objects were discovered, by using A Philips X-ray, Diffractometer type: PW1840 with Cu-Kα radiation source. The aim of this analysis is identification the corrosion compounds in order to decide whether it is authentic, stable and suited to certain kinds of treatment. To know the relation between these objects corrosion products and its burial environments in Egypt and Yemen, then compare between them. Also this information can assist in choosing the best environment for the Objects in storage or in show cases. The obtained diffraction scan given in figures 20–25 and the identified compounds represent in the Table 1.

Also XRD analysis for samples of soils, where's the objects discovered were carried as it is shown in the Figure 8 and the Table 2.

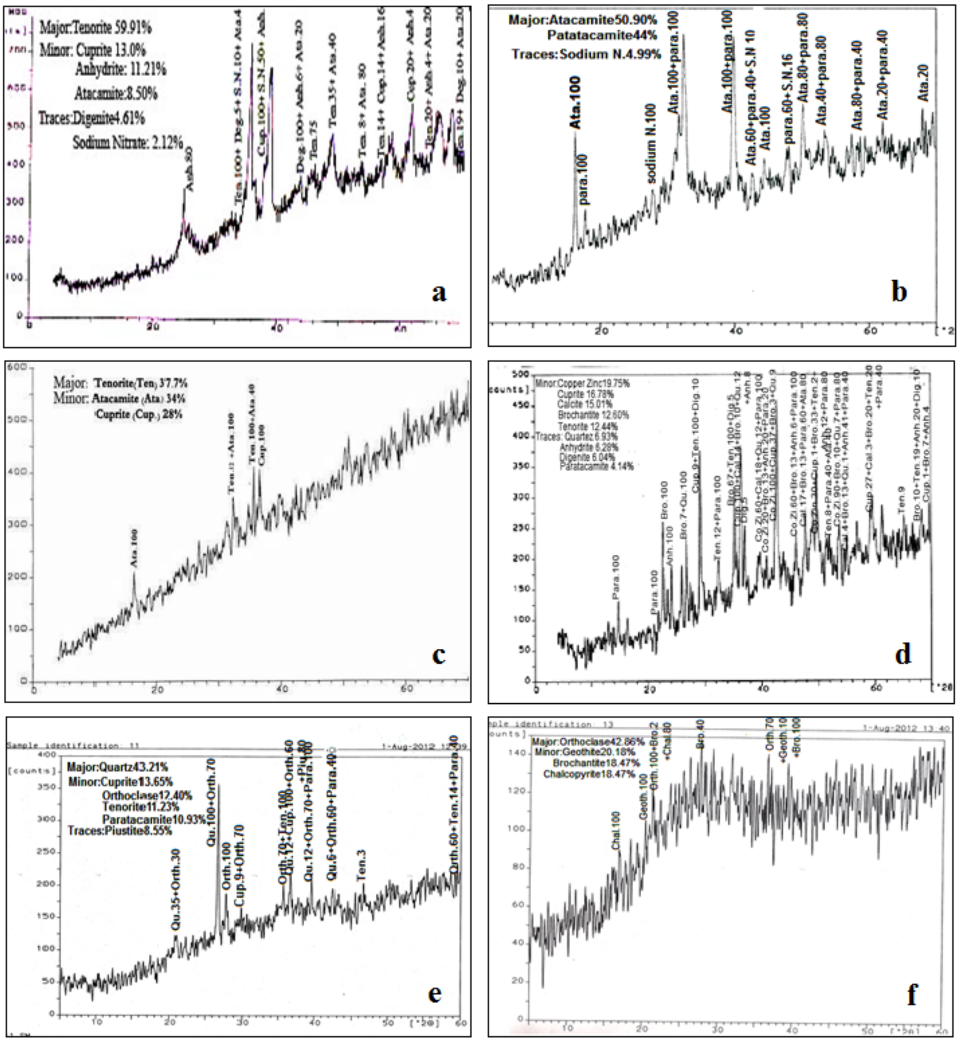

Fig. 8. The XRD Patterns of the corrosion products for: a – The God statue Tell Habua 1, North Sinai, Egypt; b – The Gods statues, Tell Habua 2, North Sinai, Egypt; c - The dagger, E Tell Atreib, Benha, Egypt; d - the Camel statue, Al-Gouf area, Yemen; e - The bracelets, Harran ,Yemen; f - The imprinting, Jahran, Yemen.

Table 1. XRD analysis results of corrosion products of the objects

Sample	Compounds		
	Major	Minor	Traces
God statue	Tenorite (CuO)	Cuprite (Cu_2O) Anhydrate ($CaSO_4$) Atacamite ($Cu_2(OH)_3Cl$)	Digenite (Cu_9S_5) Sodium Nitrate ($NaNO_3$)
Gods statues	Atacamite Cu2(OH)3Cl	Paratacamite ($Cu_2(OH)_3Cl$)	Sodium Nitrate ($NaNO_3$)
The dagger	Tenorite CuO Atacamite $Cu_2(OH)_3Cl$	Cuprite (Cu_2O)	-------
Camel statue	copper and zinc sulfide (CuS and ZnS)	Calcite ($CaCO_3$) Brochantite ($Cu_4SO_4(OH)_6$)	Quartez (SiO_2) Digenite (Cu_9S_5) Anhydrate ($CaSO_4$)
The bracelets	Cuprite (Cu_2O)	Tenorite (CuO)	Paratacamite ($Cu_2(OH)_3Cl$) Piustite (FeO)
The imprinting	Quartz (SiO_2) Orthoclase ($KAlSi_3O_8$)	Cuprite (Cu_2O) Orthoclase ($KAlSi_3O_8$) Tenorite (CuO) Paratacamite ($Cu_2(OH)_3Cl$) Geothite (FeOOH) Brochantite ($Cu_4SO_4(OH)_6$) Chalcopyrite ($CuFeS_2$)	-------

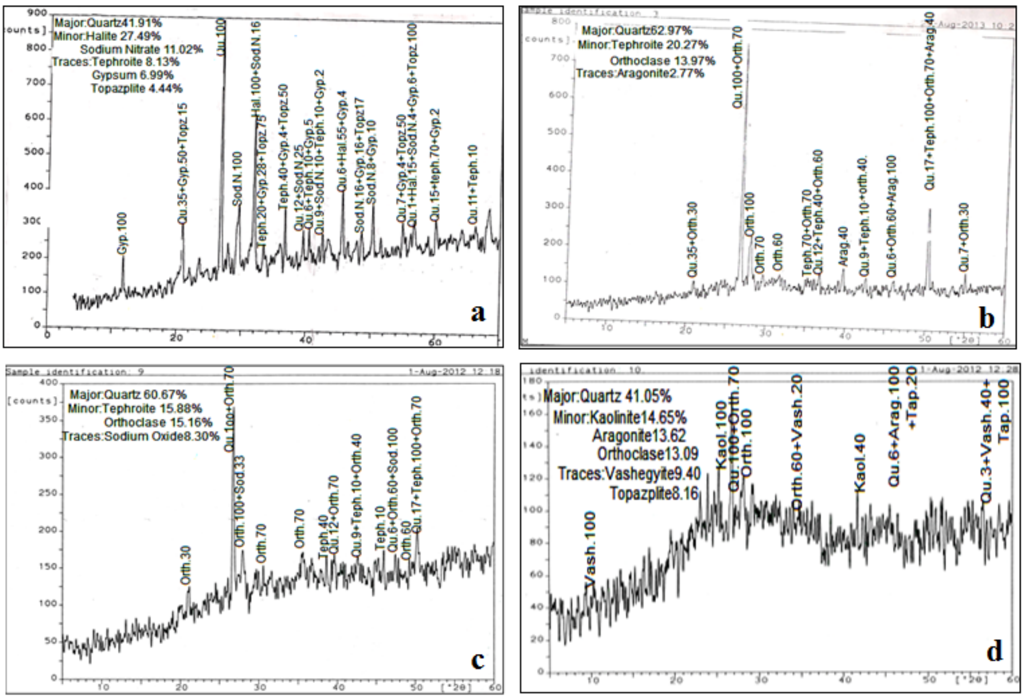

Fig. 9. The XRD patters of the soils: a - North Sinai soil, Egypt;
b - Tell-Atreib soil, Egypt; c - Harran soil, Yemen; d - Jahran soil, Yemen

Table 2. XRD analysis of the soils

Samples	Compounds		
	Major	Minor	Traces
North Sinai soil	Quartz (SiO_2)	Halite (NaCl) Sodium Nitrate ($NaNO_3$)	Tephroite (Mn_2SiO_4) Gypsum ($CaSO_4{\cdot}2H_2O$) Topazplite ($3CaO{\cdot}Fe_2O_3{\cdot}3SiO_2$)
Tell-Atreb soil	Quartz (SiO_2)	Tephroite (Mn_2SiO_4) Orthoclase ($KAlSi_3O_8$)	Aragonite ($CaCO_3$)
Harran soil	Quartz (SiO_2)	Tephroite (Mn_2SiO_4) Orthoclase ($KAlSi_3O_8$)	Sodium Oxide (Na_2O)
Jahran soil	Quartz (SiO_2)	Kaolinite ($Al_2Si_2O_5(OH)_4$) Aragonite ($CaCO_3$) Orthoclase ($KAlSi_3O_8$) Piustite (FeO)	Vashegyite ($Al_4(PO_4)_3(OH)_3{\cdot}XH_2O$) Topazplite ($3CaO{\cdot}Fe_2O_3{\cdot}3SiO_2$)

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 3.

Table 3. XRF Analysis for the objects

Elements / Samples	Cu%	Sn%	Pb%	Fe%	Zn%	As%	Total %
• God statue	89.69	6.94	0.57	0.48	0.38	0.49	100
• Gods statues	89.63	7.82	0.78	1.62	0.15	-	100
• The dagger	92.70	5.33	0.25	1.52	0.20	-	100
• Camel statue	44.20	6.02	49.01	0.14	0.63	-	100
• The bracelets	77.26	5.32	16.50	0.92	-	-	100
• The imprinting	81.22	5.17	11.63	1.12	-	0.86	100

Treatment of preservation of the objects

The Gods statues, Camel statue, the bracelets and the imprinting

The examination and analysis methods proved that the objects (God statue, three Gods statues, Camel statue, the bracelets and the imprinting) have a good metallic state, but they were covered with thick layers of corrosion products, chemical treatment was chosen, the objects were immersed completely in solution of alkaline Rochelle salt (50mg/L of sodium hydroxide + 150mg/L sodium potassium tartrate). This was done by using one Litter of distilled water, using a brush to remove the loose corrosion products, until reaching the patina (Cu_2O) it can be removed using the dilute sulfuric acid 2% by brushing. After that, the objects were washed carefully and dried by immersing it in acetone. The two parts of the first God statue were adhered by using Araldite resin; finally the objects were coated by Paraloid B72 dissolved in acetone 3% by using a brush (Figs. 10-14).

Fig. 10. The first God statue after treatment

Fig. 11. The Gods statues after treatment

Fig. 12. The bracelets after treatment.

Fig. 13. The Camel statue after treatment

Fig. 14. The imprinting after treatment

Treatment and conservation of the dagger

According to the obtained examination results the dagger partially corroded, covered with a thick layer of green corrosion products, also it was very hard brittle with many cracks on the surface and separated into two parts. However the object had a good metallic core in the middle of corrosion products, so the mechanical methods were excluded, also the chemical methods were excluded. Hence the electrical reduction method is considered prefect for treating the object as it extracts the chloride by cathodic desalination process, consolidates the object and reduces the corrosion product to metal. The method involves the use of an electrical current generated by an external source for direct current (D.C) of 1.5 -3 volts, the corroded object was connected to the negative pole whereas the stainless steel electrode was connected to the positive pole. The electrolyte used was 1.5 % Sulphuric acid. The two electrodes were cleaned up every 3 hours by brushing them. The treatment continued for 15 days, the sum of hours are one hundred hours, after completing the treatment, the object was brushed carefully with fiber glass brush, washed and dried. Finally the two parts of the object was adhered by using Araldite resin, then it was coated using salt brush with 3% Paraloid B72 dissolved in acetone to prevent further corrosion (Fig. 15).

Fig. 15. The dagger after the treatment for preservation

Results and discussions

A group of bronze objects from different archaeological sites in Egypt and Yemen were selected for study; it was distinguished two methods of ancient manufacture and two kinds of alloys for the selected objects as the following:

- The first one is a binary bronze having an average mass Tin concentration of 5.33% to 7.82% such as the dagger and the Gods statues.
- The second is a ternary bronze (copper + tin + lead), with Tin concentration of 5.17% in imprinting, 5.32% in the bracelets and 6.02% in Camel statue with a high amount of lead (11.63% in the imprinting, 16.50% in the bracelets and 49.01% in Camel statue).

The investigations serve in revealing the nature of ancient technology that the ancient manufacturer employed in ancient time to produce the selected objects, it includes Hammering, casting in molds, lost wax casting (solid or hollow casting) and cold or hot mechanical shaping. God’s statues were made of bronze alloy by wax - lost casting technique (solid casting). The dagger was made of bronze alloy; the ancient manufacturer used the two techniques, casting and hammering to make it. Camel statue, the bracelets and the imprinting were made of Lead bronze alloy and the ancient manufacturer used the casting techniques (hollow casting for the Camel, solid casting for the bracelets and the imprinting) to produce them. The ancient use of selected objects was different being artistic, ritual, common use objects and jewels.

Metallographic and Scanning Electron Microscope examinations showed the presence of pitting corrosion (Figs. 6c, 6g, 7c, 7f and 7g), lead islands disperse in the alloy contents (Fig. 6f) and crevice corrosion spreads along the edge of the metal (Figs. 7a and 8a), also the examinations showed that the dagger suffered from a partial mineralization, but it still has some of its metallic core encrusted by corrosion layers (Figs. 6d and 7d), this deterioration aspect due to the manufacture process. The brittleness therefore, might be due to the chemical composition and micro-chemical structure as well as to the ageing process, inducing a drastic change in the metallurgical and micro-chemical structure of the objects. The micro-chemical and microstructural results also show that another source of degradation of bronze archaeological objects, are their intrinsic metallurgical features whose formation is induced during the manufacturing of the objects, carried out in ancient times by reported cycles of cold or hot mechanical work and thermal treatment. These combined treatments induce crystallization and segregation phenomena of the impurities along the grain boundaries and could cause mechanical weakness and increase the extent of the corrosion phenomena.

The corrosion of the tin bronze (Cu-Sn) alloy of Gods statues consists of two layered reflect the loss of matter due to an aggressive corrosion process visible in local pits and in crevices (Figs. 6b and c, 7b and c). From the outer to the inner layer, the corrosion shows the presence of cuprous chloride layer mixes with the soil particulars and a cuprous oxide layer, which was the first layer formed on the metal surface. The corrosion layer of the leaded tin bronze (Cu-Sn-Pb) alloy of Camel statue, the three bracelets and the imprinting is distinctly visible from the alloy. Examinations show a compact two layer structure. Pitting, crevice corrosion and micro cracks are visible (Figs. 6g, 7a, 7f, 7g), also lead is visible scattered in islands in the alloy (Fig. 6f).

X-Ray diffraction analysis of the corrosion products of Gods statues, Camel statue, the bracelets and the imprinting (Table 1), revealed the presence of different minerals including Cuprite, Tenorite, Atacamite, Anhydrate, Calcite, Brochantite, Paratacamite, Copper and Zinc sulfide, and traces from sodium nitrate, Quartez and Digenite. Also analysis results of corrosion products of the dagger revealed the presence of Tenorite, Atacamite and Cuprite. The presence of Cuprite (Cu_2O) is due to selective corrosion of the main alloying element, which is re-deposited after dissolution onto the surface of the objects, thus forming a copper enriched layer. The presence of basic copper chloride is related to the sandy and saline nature of the Soil, whereas the objects were buried in Egypt and Yemen. It played an important role in their severe corrosion, this soil which is porous and changed from Sub-saturation to saturation with water, had different salt ions, specially the dangerous chlorine anion; this circulation of saline water in the soil had a serious effect on the objects.

XRD analysis of North Sinai soil, Egypt, where is the God statues were excavated revealed the presence of Quartz, Halite, Sodium Nitrate, Tephroite, Gypsum and Topazplite, it is a sandy soil. The analysis of Tell-Atreib soil, Egypt where is the dagger was excavated revealed the presence of Quartz, Tephroite, Orthoclase and Aragonite, although Quartz is the main compound in the two soils and the big similar between the Corrosion products of the Gods statues and the dagger, but the existence of Orthoclase in Tell-Atreib Soil changed its structure and properties to classify as clay/sandy soil.

XRD analysis of Harran Soil, Yemen, where is the bracelets were excavated revealed the presence of Quartz, Tephroite, Orthoclase and Sodium Oxide. The analysis of Jahran soil, Yemen, where the imprinting is excavated revealed the presence of Quartz, Kaolinite, Aragonite, Orthoclase and Piustite. The compositions of Harran and Jahran soils (Yemen) have a big similar to Tell-Atreib soil (Egypt), which can classified as clay/sandy soil, but these three kinds of soils difference from Sinai soil in its compositions, structure and properties, so the degree of deterioration and the kind of corrosion products are difference between them.

The presence of Calcite ($CaCO_3$) in the analysis results of Camel statue corrosion products from Al-Gouf area, Yemen and Aragonite ($CaCO_3$) in the analysis results of Tell-Atreib soil, Egypt and Jahran soil, Yemen is most probably formed by the reaction of soluble calcium bicarbonate with hydroxide ions produced in the cathodes reaction of oxygen, indicated that the soil usually has high carbon dioxide contents and may be chemically very aggressive because the carbon dioxide may react with water to form carbonic acid, which may attack metals directly and prevent the formation of a protective film surface. A calcareous soil may also act in a quite benign, however, especially if carbon dioxide and water produce the soluble Calcium bicarbonate. This may act to protect the bronze from corrosion, since calcium bicarbonate or hydrocarbonate is a salt of a weak acid, its aqueous solution is very alkaline, and by binding with carbon dioxide, it prevents the extensive dissolution of Cu(I) ions. At values of pH › 8 calcium bicarbonate precipitates as carbonate, and in subsequent acidic condition, this may dissolve instead of Cu(II) compound, the overall pH in dilute natural ground water is principally controlled by this $CaCO_3$-H_2O-CO_2 equilibrium.

The existence of Piustite FeO in a small amount in corrosion products of the bracelets and Geothite FeOOH in corrosion products of the imprinting as a trace, may be as a result of migration of Iron corrosion from adjacent iron objects to the selected bronze objects in the burial environment or from the buried environment itself as it is very rich with Iron compounds, this indicates the strong interaction between soil components and corrosion products.

XRF analyses of the Camel statue, the bracelets and imprinting declared that the objects were made of leaded bonze alloy (Table 3), tin exists in a reasonable amounts (6.02% in Camel state, 5.17% in the imprinting and 5.32% in the bracelets), but Lead exists in a high amounts (49.01% in Camel state, 11.63% in the imprinting and 16.50% in the bracelets). An addition of lead up to 2% improves the fluidity of the melted bronze alloy even though, a loss of mechanical properties could be induced, and toughness is sequent reduced. With higher amounts of lead, remarkably deterioration of mechanical properties is produced and the only derived advantage is the low cost of lead with respect to the more expensive and rare tin. The loss of mechanical and thermal features is well explained by the copper-lead diagram. Indeed, because lead has substantially no solid solubility in copper and copper-based alloys, if the percentage of lead in bronze is higher than a few percent, lead occurs as a dispersion of fine particles throughout the bronze [21]. The number of the lead particles and its distribution as globules in copper matrix vary as a function of the lead content and casting parameters thus giving rise to the formation of a material constituted a copper matrix where Lead islands are scattered, the resulting effect of the presence of lead on microstructure of the bronze objects. During the solidification in the copper-lead system, each component separates into a nearly pure state and has the same crystal lattices as the respective supersaturated sold solution. As a consequence, dispersed lead islands are formed in the copper matrix whose size is influenced by the cooling parameters [22]. The occurrence of this phenomenon is seen in (Fig. 6f), as a consequence of the intimate contact between (copper-tin-lead) which have different electrochemical potentials, corrosion phenomena are induced on a microscopic scale. Indeed, the contact induces the less noble metal to become anodic in a couple strongly conductive to corrosion, and a preferential dissolution of copper occurs in the less noble anodic areas. The amount of current that flows, and therefore, the extent of the corrosion, is subject to many variables, among which are the chemical-physical parameters of the burial contexts, the presence and nature of the electrolyte, and the micro-chemical structure of the alloy.

XRF analyses of the objects indicated the presence of Iron, in a small amounts ranges from 0.14% to 1.62%. This element could come from the impure copper ore or from the fluxing compound used during the smelting process, zinc is found in a small amount as impurities in Gods statues ranges from 0.15% to 0.38%, in the dagger 0.20% and in Camel statue 0.63%, thus indicating the use of Copper ores with variable content of zinc sulphide, also Arsenic is found in God statue 0.49% and in the imprinting 0.86%, respectively, thus confirming relevant differences in the alloying and refining practices. The iron, zinc and arsenic amounts indicate that the copper has been obtained from the use of a sulphide ore, which was not completely roasted and in the some cases raw refining techniques. The above reported results indicate the presence of variable amount of impurities most of which could be reduced to acceptable levels quite easily by melting the copper or the bronze in an open crucible and allowing the unwanted elements to oxidize, to float to the melted surface and be skimmed off. Therefore, the results indicated that refining processes have not always been carried out before casting, and the row bronzes were used for producing same of the selected objects.

The chemical cleaning carried out for removing the external crust corrosion products, encrustations and the phases coming from the soil cannot ensure the complete removal of corroding agents such as Cl and S that could be yet present within the patina thus inducing a further degradation. Moreover, the above discussed results demonstrate that the removal of Cu(II) compounds and Cuprite (Cu_2O) layer from the surface could exposed the copper chlorides present under the Cu_2O layer, thus inducing the cyclic reaction of copper corrosion and therefore, inducing the partial disfiguration of the artifacts. Therefore, particular attention must be paid before and during the removal of surface encrustations and corrosion products layers in particular of cuprite in order to avoid ensuring copper chlorides to humidity and oxygen. The role of cuprite layer has been discussed by V.F. Lucey [23] and has been considered to be acting as an electrolytical membrane allowing the transport of anions such as chlorine (Cl^-) and oxygen (O^{2-}) anions inward and cuprous ions outward. Indeed, the presence of copper chlorides in the archaeological artifacts indicates a noticeable transportation of chlorides from the soil through the permeable corrosion products layers to the internal zone and remaining Cu-base matrix. The accumulation of chloride ions can be interpreted as an autocatalytic reaction that facilitates the oxidation of copper resulting also in an accumulation of chloride ions and in the formation of cuprite and cuprous chloride, as described in details by [24-32]. These considerations show that uncompleted knowledge of corrosion products and degradation mechanisms as well as inappropriate preservation materials and cleaning treatments, could not stop the degradation phenomena and aren't able to ensure a long-term chemical-physical stability for the archaeological bronze artifacts.

The electrical reduction method is considered the best treatment method, which can be employed when a good continuous core of a metal remains in the object, as the electrical reduction method convert the corrosion products to metal, extracts the chlorides and improve the mechanical strength of the objects, it is preferred to follow this method by a thermal treatment to return back the physical and mechanical properties of the object. During treatment the metallic objects by the electrical Reduction method , we must brush the object, when we find a difficulty in making a good electrical contact with the corroded object to scrap away the rust to expose some un corroded metal for this purpose. Also we must use a very low current value to keep the cathodic potential at a stable value 1.5 volt to limit the evolution of hydrogen.

Conclusions

From the present study we concluded the following:

- In an oxygenated corrosion medium, the main phenomenon involved in bronze corrosion is copper selective dissolution from copper solid solution (α-phase), the corrosion process can not be assimilated to destannification, as it was assumed before, but corresponds to decupification.
- The investigations carried out on different archaeological bronze samples have shown that a strong relationship exists between the type of the surrounding environment and corrosion products, as there are two different types of corrosion observed, the first layer is cuprite (Cu_2O) with its red/brown colors , which must be formed at first on the metal surface before the other corrosion compounds are formed, the second type is the basic copper chloride which is related to the presence of the chlorine ion in the medium.
- ME, SEM and XRD results show the occurrence of selective localized or general chlorine corrosion phenomena induced also by the separation of the alloying elements, which creates reactive electrochemical areas.
- The chemical composition, the micro-chemical structures and metallurgical feature of the objects have been determined and can be used to identify some technological aspects of the ancient manufacturing processes.
- The morphology of the surfaces and the elemental compositions of the corrosion products depend strongly on the chemical composition of the alloys.
- The electrical reduction method is considered the best method which can be used for treating the partially corrosion metallic objects, when a good continuous core of metal remains, as it converts the corrosion products to metal, extracts the Chlorine ions and improve the mechanical strength of the object, it can be followed by a thermal treatment.
- Corrosion control wouldn't be complete without mentioning, water controlling, these gadgets are usually promoted on the basis that they will stop corrosion, prevent scaling and destroy bacteria. The object was treated by cleaning and removing the corrosion factors. The environments must be dried and cleaned to prevent pollution.
- Inhibitors and coatings were usually used to prevent further corrosion.

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