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CONSERVATION TREATMENT AND ANALYTICAL STUDY OF EGYPTIAN GILDED BRONZE STATUE OF SEATED OSIRIS

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Abstract

An interesting example of a bronze seated Osiris statue dated back to the Late Period (664-332 B.C), preserved in the store museum of Kom Oshim, Fayoum, EGYPT. The hollow-casting process was used in the statue manufacturing technique. A detailed characterization of the statue was carried out through USB digital microscope, metallographic examination, portable X-ray fluorescence, X-ray diffraction and scanning electron microscope with energy dispersive spectroscopy. The results revealed that statute has been made of lead bronze alloy with low tin and high lead. EDS results showed that the gold leaf contains more than 90%wt. Au content. The corrosion products identified by XRD are cuprite, malachite, azurite and atacamite. Pre-treatment, a consolidation and fixing processes were carried out by using Paraloid B72 3% in acetone to ensure that the gilding adhered firmly to the surface. Mechanical cleaning was accomplished via safe hand tools to remove corrosion products and soil encrustations and avoid losing the gold remains. BTA 3% in alcohol was applied in the areas of active corrosion, then two layers of permalac were applied.

***Keywords**: Conservation treatment; Analytical study; Gilded bronze statue; Seated Osiris.*

Introduction

The gilded seated Osiris was cast with the lost wax method; an interior core filled the hollow. The core is often made of clay, to prevent the metal filling the whole cavity. This technique is used to reduce the weight of the object or to economize on the quantity of metal [1, 2]. In ancient times, gilding was used as a method of decorating the surface of a less precious metal, where it is fixed either mechanically or physically. Gold leaf differs from gold foil in being much thinner. The manufacturing of gold leaf was difficult before perfection of the purification methods [3-10]. In Egypt, Gold beating is a specialized craft going back to the New Kingdom Period. The wall painting in the tomb of Rekhmire depicts (Thebes, (1554-1080 B.C)), gold beaters used hammer stones to beat the gold foil between sheets of gold beater's skins [11]. Animal glue and egg-white have been used to attach gold leaf to the metal surface [12]. Leaf gilding can be also done by heating to take place inter-diffusion of the gold and the underlying metal [7, 13].

The corrosion process of gilded metals occurs specifically in the highly porous and cracked areas of the gold layer. The electrochemical corrosion rate of the metal below the gilding layer is very high, because gold provides an area of cathodic reactions such as oxygen

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reduction, and the anode reaction increases when the most reactive metal is exposed to the surrounding environment through the pores in the gilding layer, and the formation of pits increases with continuous corrosion. Blistering of the gilding layer is a result of the deposition of the corrosion products. Detachment of this layer from the metal surface could be occurred by the progressive swelling of corrosion products [14-24].

The conservation of corroded gilded bronze presents a number of difficulties concerned both with the preservation of technological evidence and with the stability of the object itself. Gilding exists as a thin, disrupted and discontinuous layer enclosed in a hard matrix of copper oxides and soil sediments. Removing the corrosion crusts by mechanical means without eliminating the gold layer is a very difficult task. Another problem that has to be solved is the presence of copper chlorides underneath the gold layer. It is advisable to eliminate them to avoid a future degradation of the metallic core but on the other hand, the gold leaf is often supported by the chloride layer [21, 25, 26].

Before cleaning, it is necessary to strengthen the gilding layer which may be lost during removing the underlying corrosion products. A consolidant such as Paraloid B72 3% in acetone may be employed to fix the gilding layers which have become detached. It is sometimes possible to apply the adhesive in solution and allow capillary action to spread the adhesive under partially detached flakes. Careful surface cleaning can then be carried out without the risk of losing parts of the gilding layers [16, 25].

There are different opinions about conservation techniques of gilded metal objects. Mechanical cleaning is the preferred option in these cases. Where the use of chemical solutions might change the chemical composition of the remaining layers and can penetrate the patina and dissolve it. Therefore, those procedures can somehow damage the patina supporting the gold layer [26-28]. On the other hand, Jedrzejewska [29] stated that mechanical cleaning is not advised, because gold adheres very firmly to layers on top of it and less so to underlayers, and so has the tendency to come off with the removed deposits if mechanical cleaning is attempted. Even with gold adhering well to the underlayer there always remains the risk of scratches and abrasions from cleaning tools.

For ideal preservation, bronze objects can be stored in stable conditions with the other metallic objects, as long as the humidity does not exceed 55%, but if it exceeds this level, these objects should be transported to a single cabinet where RH can be kept low with a dehumidifier. If it shows any signs of active corrosion (bronze disease), it should be stored individually at a relative humidity below 35% and not exceed 20°C [14, 30]. In general, cuprous chloride remains stable in the absence of both oxygen and moisture [31]. The presented research provides a conservation strategy and investigation study of the gilded bronze statue of seated Osiris.

Experimental part

Materials

In this work, the object was excavated from Ehnasya (Ehnasya; Ancient Egyptian: Henen-Nisut) in 1956, preserved in the store museum of Kom Oshim, Fayoum, EGYPT, with No. 26 from Naguib Farg's records. It is dated to the Late Period (664-332 B.C), measures 13.5cm height and 5.5cm width and 2mm in thickness, and weighs 185 grams. Gilded areas remain on the face and chest, but there is no evidence of gilding on the back of the statue, as shown in figures 1a and b, and 2. A tang underneath buttocks would have been used to secure the statue to a base made from metal or wood, usually there is another one underneath the feet, but the pair of legs are broken as shown in figure 3. The eyes are inlaid, where the eyeball would typically have been made from marble, although other materials found in this context include white opaque quartz, glass or bone. A white fill in the center, which may be cement, possibly used to hold an eyeball insert in place [32]. We were unable to identify the composition of the inlaying material, because of the difficulty of taking a sample.

Fig. 1. A and B: The statue of gilded seated Osiris before conservation treatment

Fig. 2. Detailed view shows the gilding residues are embedded in corrosion products and soil inclusions

Methods and techniques

Microscopic Investigations. Gilded bronze statue was investigated under lens magnification to detect the gilding remnants and corrosion forms, as shown in figure 4. The USB digital microscope was used to identify the surface morphology of the bronze patina [33, 34].

pXRF. The Bruker S1 TITAN and TRACER 5i Handheld XRF Spectrometer was used to determine the elemental chemical composition of bronze alloy and of the gilding composition.

Metallography. Cross-section was examined through the Leco L31 metallographic microscope to determine the microstructure before and after chemical etching. It was first polished with SiC abrasive paper and then polished with a ½ µm alumina suspension. Sample was examined both in unetched and etched conditions. The etching solution was prepared using an alcoholic ferric chloride solution (240mL ethanol, 60mL hydrochloric acid and 20g ferric chloride).

SEM-EDS. The cross-section sample was examined under the Inspect S50 Scanning Electron Microscope, FEI company (SEM) with energy dispersive spectroscopy (EDS) to identify the alloy microstructure, and to assess the composition of the manufacturing alloy and gold layer.

XRD. X-ray diffraction (XRD) was accomplished by D8 advance X-ray diffractometer (Bruker, Germany) to identify the composition of corrosion products and the inner core minerals of the hollow cast statue.

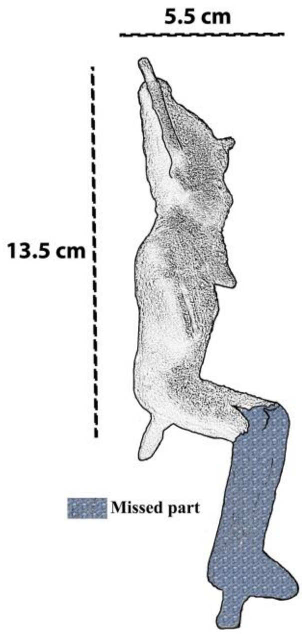

Fig. 3. A drawing shows the statue missed part

Results and Discussion

Morphology of gilded bronze surface

A detailed examination showed that gilding layers were observed on various areas in the front, while they were not found in the back as shown in figure 5a and b. It is likely that the statue was completely gilded, but that when it was lying down on its back in the soil, the gilding was lost. The eyes were inlayed with a white stone while the eyebrows were inlayed with a lime-paste.

Red,green and blue corrosion products were observed on the surface as shown infigure 5c-e. Cracks are clearly visible on the surface of the head as shown in figure 5f. Cross-section was examined by digital and SEM microscope showing the following layers: gold leaf, cuprite and alloy, the green corrosion products have been observed in the internal layer, as shown in figures 6 and 7. It can be noted that copper chloride and copper oxide layers are the usual components found below the gilding layer, and soil inclusions are found above the gilding layer, which makes it very fragile [25, 35]. The broken and open bottom provided a good opportunity for identifying the chemical structure of the interior core.

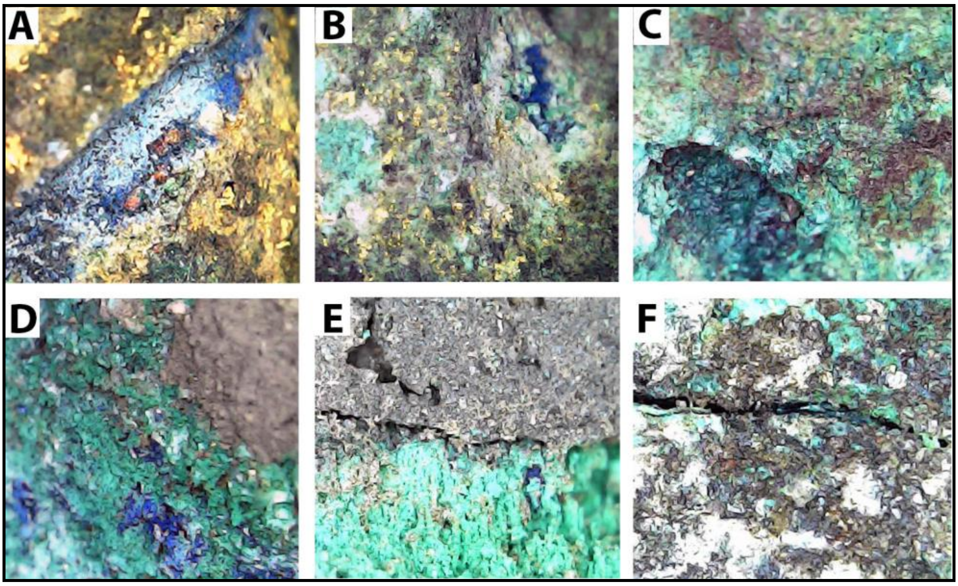

Fig. 5. Microscopic image of the surface morphology: A and B - gilding residues are embedded inside corrosion products and soil deposits; C and D - blue and green corrosion incorporated with soil deposits covering the surface; E - pale green corrosion products are existed beside the interior core; F - cracks in the head from the back

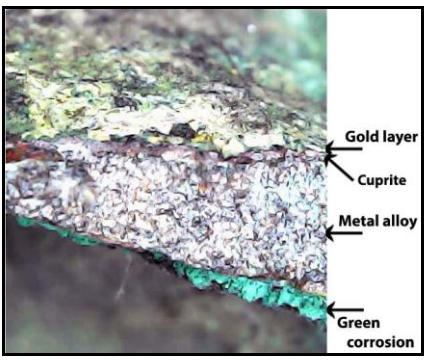

Fig. 6. A cross-section of the gilded statue showing a cuprite layer is found below the gilding layer. Green corrosion products is found in the inner surface

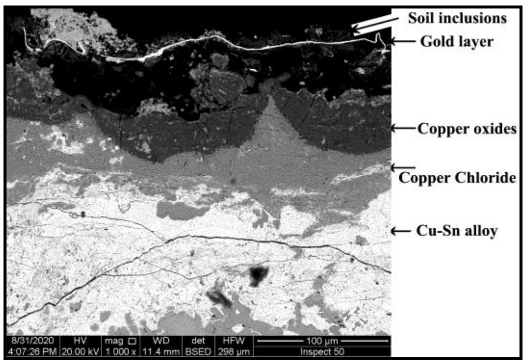

Fig. 7. SEM image of a cross section from the gilded bronze statue shows the gold layer found on the top of corrosion products

Bronze alloy microstructure

A cross-section sample was subjected to metallographic and SEM investigations, and the results are presented in figures 8 and 9. It can be noted that a matrix composed of α-phase (light colored) and δ phase (dark colored) of the bronze alloy, lead particles (black colored) distributed between the dendrites because of the limited solubility of Pb in Cu-Sn alloy. The abundant segregated lead appears as masses (40x50μ) all over the bronze matrix which indicates the slow cooling rate of the alloy [36-38].

Lead does not really affect the solidification structures, since it does not alloy with the copper or tin, it remains as small globules throughout the structure, which can be small and well distributed in low-lead bronzes or large and irregular in highly leaded bronzes [39, 40]. The addition of lead to the copper and tin lowers the melting point and greater than 13% increases the metal fluidity. Thus, the casting is much better, which explains the use of this alloy in finely detailed artistic objects, which do not require special mechanical features [36, 41-44]. Elemental mapping for the main chemical elements found in the metal core is shown in figure 10. It can be noted that copper and tin metals are extremely homogeneous mixtures, but lead is immiscible.

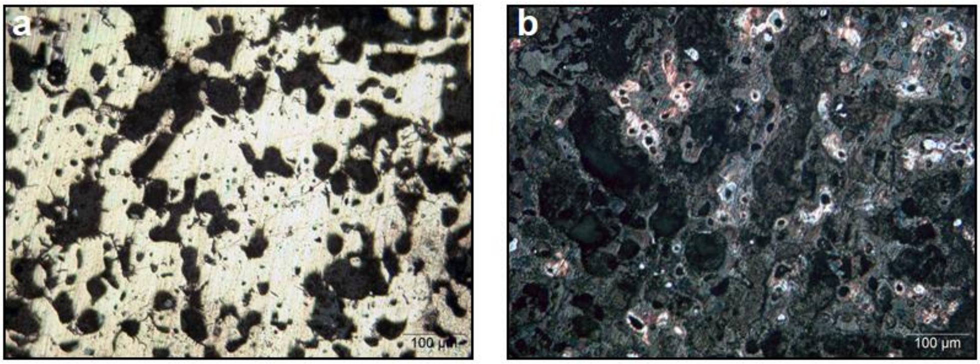

Fig. 8. Metallographic images showing the bronze matrix contains α -phase, (α + δ) eutectoid and Pb irregularly shaped dispersed inclusions: **a.** Un-etched sample; **b.** etched sample

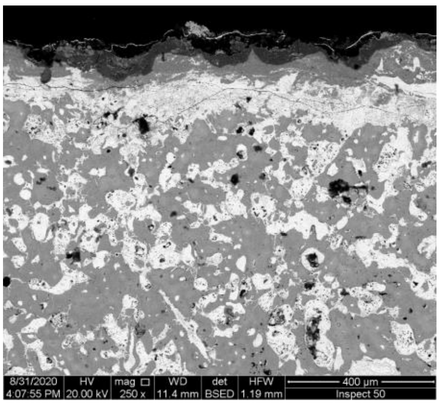

Fig. 9. SEM image shows the bronze matrix contains α -phase, (α + δ) eutectoid and Pb irregularly shaped dispersed inclusions

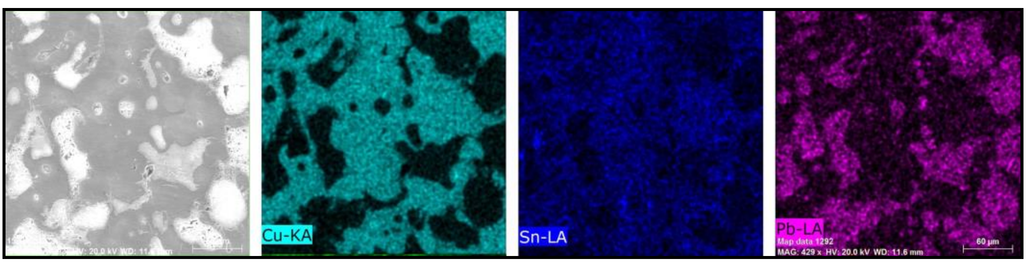

Fig. 10. Elemental map for the main chemical elements present in the alloy core

Chemical composition of bronze alloy and gold layer

SEM/EDS investigations of the alloy microstructure are given in (Fig. 11 and Table 1). Figure 12 shows non-destructive in situ analysis by pXRF, the analysis results of the corroded gilded bronze are given in Table 2.

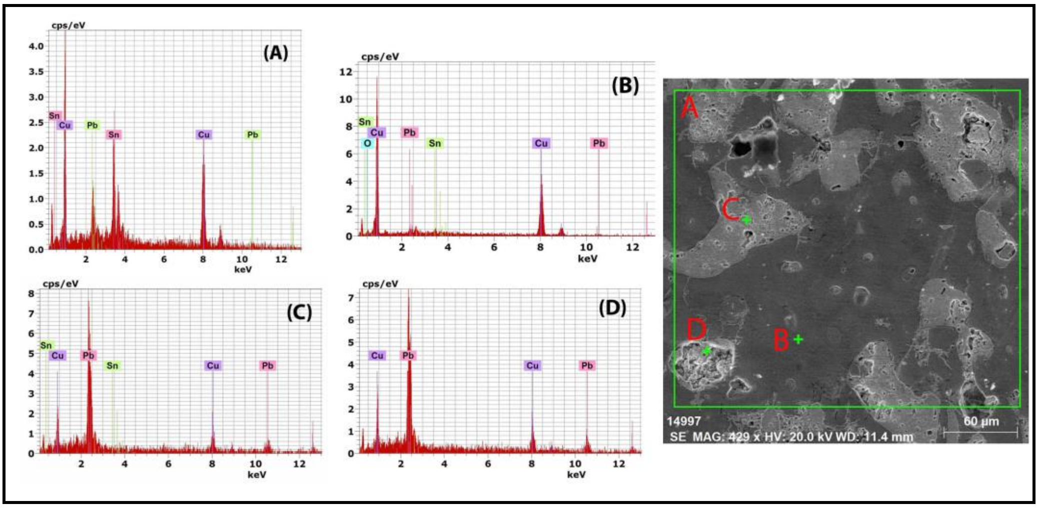

Fig. 11. SEM image shows the microstructure of the bronze alloy, a-d: the corresponding EDS analysis of some phases of the alloy

Table 1. EDS analysis of different spots in the alloy and the gold layer

Element wt% / Spot	Cu	Sn	Au	Pb
A	70.84	3.12	---	26.04
B	90.14	3.48	---	6.38
C	20.36	1.08	---	78.56
D	21.69	---	---	78.31
E	4.07	1.12	92.32	2.49

Table 2. XRF results the elemental chemical composition of the alloy (wt.%)

Element	Front	Upper	Lower	Back
Mg	3.081	1.645	2.166	2.697
Al	0.927	0.89	0.312	3.901
Si	6.434	9.966	3.582	10.952
P	0.182	0.453	0.182	0.57
Cl	0.151	0.345	0.36	1.896
K	0.298	0.223	0.088	1.463
Ca	4.211	4.322	3.325	3.385
Fe	1.027	0.568	0.318	4.867
Cu	61.547	66.226	73.808	57.582
Sn	0.852	0.601	0.795	0.458
Au	5.298	1.811	1.958	---
Pb	15.991	12.949	13.105	12.228

According to Table 2, this alloy was manufactured with high lead content (12.23 - 16.00 %wt.), and low tin content (0.46 - 0.85 %wt.). Gold is detected ranging from 1.81 %wt. to 5.30 %wt. Silicon, calcium, chlorine and magnesium were detected by pXRF analysis of an uncleaned surface. The presence of these elements can be attributed to the soil sediments that covered the statue due to burial in the soil. Chlorine can be also attributed to the presence of soluble salts in burial environment.

XRF results of the back show high contents of Si, Ca, and Cl, indicated that the statue was lying on its back in the soil, likely leading to the complete loss of gilding. The results extracted from elemental analysis (EDS and XRF) indicated that the statue manufacturing alloy is a high leaded tin bronze. A number of researchers investigated a group of ancient Egyptian statues, they have found that the statues are made of lead bronze alloy. This indicates that, in this period of ancient Egypt, the leaded bronze alloy was extensively used for making statues [37, 45, 46]. According to Ogden [47], the thinner walled and more precise hollow castings appear to be tin-bronzes with minimal lead. However, high lead content is typically a Late Period phenomenon that continued into the Ptolemaic period, when over 20% is not unusual, and over 30% is reported in some instances.

SEM image shows the gilding layer measuring 22µ thick in average, as shown in figure 13. EDS analysis shows the elemental composition of the gilding layer as shown in Figure 13 and Table 1. It consists of more than 90% wt. Au. This purity may be indicative of refined gold. The Cu, Sn and Pb content isn't actually a part of the gilding metal, it is derived from the underlying bronze, since it is very difficult to prepare gold leaf containing this much copper, tin and lead [45]. Ghoneim [49] investigated gilded group statues and found that the gilding was made of gold leaf (>85%).

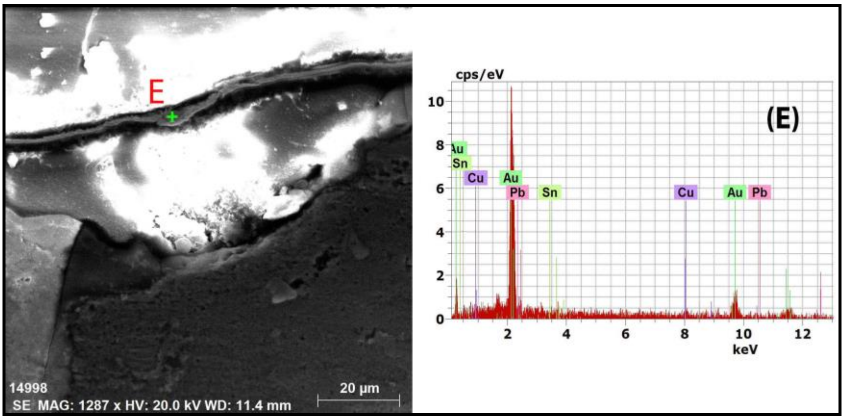

Fig. 13. SEM image and the corresponding EDS analysis of the gilding layer

The corrosion mechanism

The main corrosion products identified by XRD were: atacamite (Cu(OH)CI), cuprite (Cu_2O), malachite, ($Cu_2(CO_3)(OH)_2$) and azurite ($Cu_3(CO_3)_2(OH)_2$), Table 3. Cuprite and malachite are the prevalent corrosion products formed on copper alloys during soil burials [26, 50-52]. In the burial environment, the presence of carbonates can lead to the formation of copper (II) carbonate hydroxides such as green malachite and blue azurite. Malachite tends to form on copper alloys in contact with ground waters containing dissolved carbon dioxide, and azurite is preferred under drier conditions with high carbon dioxide levels.

Since chloride ions are present in the burial environment, the copper (I) chloride nantokite may also be present. Covering these copper (I) compounds are outer layers of green or blue copper (II) compounds, consisting of one or more copper (II) salts [50]. Copper (II) hydroxy chloride patinas are considered to be one of most dangerous types of corrosion, due to low stability caused by the pressure resulting from the growth of hygroscopic crystals. They expand in volume on conversion to one of the coppers trihydroxychlorides as paratacamite then turn to atacamite. This creates physical stress resulting in cracking or fragmentation [53, 54].

The presence of cracks and the open broken part, as shown in figures 14 and 15, is due to loss of mechanical properties, chemical structure and burial conditions. Loss of mechanical properties is a result of the high lead percentage. The presence of lead plays a vital role in the corrosion mechanism; during the alloy solidification process it tends to form intergranular corrosion where the processes of corrosion are promoted [51].

Fig. 14. Cracks in the head

Fig. 15. the statue broken Knee

Table 3 also shows the XRD results of the interior core. It is composed of quartz (SiO_2), gypsum ($CaSO_4{\cdot}2H_2O$) and iron hydroxy-oxides (Goethite α.FeOOH and Feroxhyte δ′-FeOOH), where paratacamite is presented due to the copper of bronze surface. The interior core was most usually made from sandy clay loam with an organic binder like dung or chaff or carbon which gets from bone dust or sawdust, due to its ability to penetrate through the mold holes after burning [47, 56]. Blackened cores of this type are typical of Egyptian and other ancient hollow-cast copper alloy objects [47].

Table 3. XRD result of the interior core

Sample	Crystalline component	Intensity	Chemical structure	d-spacing	Card number
Corrosion Products	atacamite	Major	Cu(OH)CI	5.03, 2.77	02-0146
	cuprite	Minor	Cu_2O	2.46	05-0667
	malachite	Traces	$Cu_2(CO_3)(OH)_2$	2.86	10-0399
	azurite		$Cu_2(CO_3)(OH)_2$	3.51	11-0682
Interior Core	Quartz	Major	SiO_2	3.35	46-1045
	Gypsum		$CaSO_4.2H_2O$	4.29	33-0311
	Paratacamite	Minor	Cu(OH)CI	2.28	15-0694
	Goethite		α.FeO(OH)	2.46	17-0536
	Feroxhyte	Traces	δ′-FeOOH	1.67	13-0087

Conservation treatments

Mechanical cleaning methods, complemented with the advance of optical instruments, are today considered a very suitable solution for the cleaning of gilded objects. The use of optical instruments such as binocular microscopes is a must when working on these small objects, where intact gilding might appear underneath the visible surface any time during the cleaning process [20].

The aim of the cleaning procedures is to preserve all the gilding remains and recover the surface details. Conventional techniques of cleaning are such a safe to detect and recover all the gilding remains and surface details which cannot be seen due to the rich-corrosion products with soil deposits. Treatment procedures of gilded metal objects mainly depend on the used gilding technique, in terms of the thickness of the gilding layer and its adhesion to the metal surface. If gilding is applied by using gold foil fixed mechanically by crimping it around the metal, in this case, it is strong enough to withstand the cleaning methods used to remove the outer corrosion layers. But if the gilding is applied by using gold leaf fixed directly on the surface with an adhesive or by diffusion and flacked off, in this case, it couldn't withstand the different cleaning methods. So, the decision to use any of the treatment methods depends on the object condition, which is determined by the restorer/conservator scientific [14].

Conservation treatment was totally accomplished using fine and simplest manual tools using surgical scalpel blades and an organic brush under lens magnification with a lighting source to remove encrustations with great cautious, as shown in figure 16. Prior to mechanical cleaning, a consolidation and fixing processes were carried out by using Paraloid B72 3% in acetone to ensure that the gilding is adhered to the surface. There is potential for further cleaning of the surface, especially on the back of the statue where considerable amounts of burial deposits are still present that appear to cover all the surface. So, after making sure that there is no gilding residue on the back of the statue, the rotary vibration tool was used to remove all encrustations and show all the details. The statue edges were strengthened from the inside by using Paraloid B72 70% in acetone to prevent further fracture of the statue's body, as shown in figure 17.

Fig. 16. Cleaning processes under lens magnification

Fig. 17. Consolidation of the statue edges from interior

BTA 3% in Alcohol was applied in the areas of active corrosion. Finally, the protection process of Osiris statue was accomplished using two layers of Permalac, as shown in figure. 18.

Fig. 18. The statue after treatment processes.

Permalac (N-Butyl acetate) is an air-drying lacquer in less than 5 minutes manufactured by Peacock Laboratories in 1995 [57]. The statue was packed individually in rigid polyethylene box which is well padded with acid- free tissue. Before padding the box, a layer of silica gel was inserted in the bottom, which provides an appropriate temperature and relative humidity, until the statue will be transported to a controlled environment [58].

Conclusion

The hollow cast bronze statue composed of Cu-Pb-Sn ternary alloy referring to bronze alloy. The gilding technique was carried out by using gold leaf with >90%.wt. Au. The main corrosion products identified by XRD were atacamite, cuprite, malachite and azurite. Based on the corrosion rates, the statue corrosion mechanism is due to long-term burial in corrosive soil rich in water and dissolved ions. Microscopic examination showed that the corrosion products are located underneath the gilding or in some areas are found over the gilding. The presence of cracks and the broken part is due to loss of mechanical properties, chemical structure and burial conditions. Mechanical cleaning is the preferred method for treating gilded corroded objects, because chemicals can penetrate into the patina supporting the gold and dissolve it. The statue edges were strengthened from interior by using Paraloid B72 70% in acetone to prevent further fracture of the statue's body. BTA and permalac were applied to guarantee the statue's long-term preservation.

Abbreviations

B.C: Before Christ;
SEM: Scanning Electron Microscope;
EDS: Energy Dispersive Spectroscopy;
XRD: X-Ray Diffraction;
XRF: X-Ray Fluorescence;
***p*XRF:** Portable X-Ray Fluorescence;
RH: Relative Humidity;
BTA: Benzotriazole;
SiC: Silicon Carbide Paper.

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References

[1] M.H. Garland, C.O. Bannister, **Ancient Egyptian Metallurgy**, Charles Griffin and Co. ltd., London, 1927.
[2] H. Hodges, **Artifacts, An Introduction to Early Materials and Technology**, London, Bristol Classical Press,1964.
[3] W.A. Oddy, *Gilding through the ages: An outline history of the process in the old world*, **Gold Bulletin**, 14, 1981, pp. 75-79.
[4] W.A. Oddy, *Gilding of metals in the old world*, **Metal Plating and Patination**, (Editos: S. La Niece and P. Craddock), Butterworth, London, 1993, pp. 171-181.
[5] J. Ogden, *Aesthetic and technical considerations regarding the colour and texture of ancient gold work*, **Metal Plating and Patination**, (Editors: S. La Niece and P. Craddock), Butterworth, London, 1993, pp. 39-49.
[6] K. Anheuser, *Archaeotechnology: The practice and characterization of historic fire gilding techniques,* **JOM-Journal of the Minerals Metals & Materials Society, 49**(11), 1997, pp. 58-62. DOI10.1007/s11837-997-0015-6.

[7] W.A. Oddy, *A history of gilding with particular reference to statuary*, **Gilded Metals: History, Technology and Conservation**, (Editor: T. Drayman-Weisser), Archetype Publications, London, 2000, pp.1-19.
[8] P.S. Griffin, *The selective use of gilding on Egyptian polychromed bronzes*, **Gilded metals: History, Technology and Conservation**, (Editor: T. Drayman-Weisser), Archetype Publications, London, 2000, pp. 49-72.
[9] A. Adriaens, *Non-destructive analysis and testing of museum objects: An overview of 5 years of research*, **Spectrochimica Acta**, **60**, 2005, pp. 1503 – 1516.
[10] E. Darque-Ceretti, E. Felder, M. Aucouturier, *Foil and leaf gilding on cultural artifacts; forming and adhesion*, **Materia-Rio De Janeiro, 16**, 2011, pp. 540-559. DOI10.1590/S1517-70762011000100002.
[11] B. Scheel, **Egyptian Metalworking and Tools**, Shire Egyptology, Great Britian, 1989.
[12] A. Lucas, **Ancient Egyptian Materials and Industries**, London: St Ann's Press; 1926.
[13] S. Gänsicke, R. Newman, *Gilded silver from ancient Nubia*. **Gilded Metals: History, Technology and Conservation**, (Editor: T. Drayman-Weisser), Archetype Publications, London, 2000, p.83.
[14] L. Selwyn, *Corrosion chemistry of gilded silver and copper*, **Gilded metals: History, Technology and Conservation**, (Editor: T. Drayman-Weisser), Archetype Publications, London, 2000, pp. 22-23.
[15] G. Alessandrini, G. Dassù, P. Pedeferri, G. Re, *On the Conservation of the Baptistery Doors in Florence*, **Studies in Conservation**, **24**, 1979, pp. 108-124.
[16] P. Fiorentino, M. Marabelli, M. Matteini and A. Moles, *The Condition of the 'Door of Paradise' by L. Ghiberti. Tests and proposals for cleaning*, **Studies in Conservation**, **27**, 1982, pp. 145-153.
[17] E. Angelini, S. Grassini, T. De Caro, G.M. Ingo, *Survey of the Italian archaeology precious metal collections: characterization of the patina and study of the degradation phenomena*, **Strategies for Saving our Cultural Heritage**, (Editors: V. Argyropoulos, A. Hein and MA. Harith), TEL of Athens, Athens, 2007, pp.184-188.
[18] G.M. Ingo, *Microchemical investigation of ancient silver and gold plated objects: coating techniques and degradation mechanisms*, **Strategies for Saving our Cultural Heritage**, (Editors: V. Argyropoulos, A. Hein and MA. Harith), TEL of Athens, Athens, 2007, pp. 9-13.
[19] A. Guisti, M. Matteini, **The Gilded Bronze Paradise Doors by Ghiberti in the Florence Baptistery**, International Tagung zur Metallrestayrierung veranstaltet vom Bayerischen Landesamt fűr Denkmalpflege und vom Deutshen Nationalkomitee von ICOMOS, Műnechen, 1997, pp. 47-51.
[20] J. Barrio, L. Campanella, M. Ferretti, A.I. Pardo, M. Retuerce, *Objects from the ancient site of Qalat Rabah (Calatrava la Vieja): a case study on the characterization and conservation of Islamic gilded bronze from Spain*. **Metal 04: Proceeding of the International Conference on Metal Conservation**, (Editors: J. Ashton and D. Hallam), National Museum of Australia, Canberra, 2004, pp. 173-184.
[21] J. Barrio, J. Chamon, M. Ferretti, M. Arroya, A.I. Pardo, A. Climent, M.D. Ynsa, P.C. Gutierrez, *Study of the conservation problems of the archaeological gilded metals from the islamic site of Qalat Rabah*, **Metal 07: Proceedings of the ICOM-CC Metal WG Interim Meetin, (**Editor: C. Degrigny), Rijksmuseum Amsterdam, Amsterdam, 2007, pp. 10-16.
[22] R. Borges, I. Tissot, A.I. Seruya, R.J.C. Silva, S. Fragoso, B. Maduro, A. Pai, *Gilding and silvering surface decoration techniques, and copper provenance studies of the tomb of D. Afonso of Portugal (15th century)*, **X-Ray Spectrometry, 37**(4), 2008, pp. 338-345.

[23] I. Sandu, O. Mircea, A.V. Sandu, I. Sarghie, I.G. Sandu, V. Vasilache, *Non-invasive Techniques in the Analysis of Corrosion Crusts Formed on Archaeological Metal Objects*, **Revista de Chimie**, **61**(11), 2010, pp. 1054–1058.
[24] I.G. Sandu, O. Mircea, V. Vasilache, I. Sandu, *Influence of archaeological environment factors in alteration processes of copper alloy artifacts*, **Microscopy Research and Technique, 75,** 2012, pp. 1646–1652. https://doi.org/10.1002/jemt.22110.
[25] D.A. Scott, *The deterioration of gold alloys and some aspects of their conservation*, **Studies in Conservation**, **28**, 1983, pp. 194-203.
[26] D.A. Scott, **Copper and Bronze in Art: Corrosion, Colorants and Conservation**, Getty Conservation Institute, Los Angeles, 2002.
[27] H. Jedrzejewska, *The conservation of ancient bronzes*, **Studies in Conservation**, **9**, 1964, pp. 23-31.
[28] A.V. Rossetti, V. Marabelli, *Analyses of the Patinas of a Gilded Horse of St Mark's Basilica in Venice: Corrosion Mechanisms and Conservation Problems*, **Studies in Conservation**, **21**, 1976, pp. 161-170.
[29] H. Jedrzejewska, *A corroded Egyptian bronze: cleaning and discoveries*, **Studies in Conservation**, **21**, 1976, pp. 101-114.
[30] E.B. Banning, **The Archaeologist's Laboratory: The Analysis of Archaeological Data**, Springer International Publishing, New York, 2020.
[31] M. Rimmer, D. Thickett, D. Watkinson, H. Ganiaris, **Guidelines for the Storage and Display of Archaeological Metalwork**, English Heritage, Swindon, 2013.
[32] G. McArthur, J.H. Taylor, P. Craddock, *The conservation and technical investigation of a hollow-cast Egyptian bronze*, **British Museum Technical Research Bulletin**, **9**, 2015, pp. 11-120.
[33] O. Mircea, I. Sandu, V. Vasilache, A.V. Sandu, *Study of the atypical formations in the corrosion bulks of an ancient bronze shield, by optical and electron microscopy*, **Microscopy Research and Technique, 75**, 2012, pp. 1467–1474. https://doi.org/10.1002/jemt.22090.
[34] O. Mircea, I. Sandu, V. Vasilache, A.V. Sandu, *Research on Atypical Formations from Corrosion Bulks of an Ancient Bronze*, **Revista de Chimie, 63**, 2012, pp. 893–899.
[35] M. Sawada, *A new technique for removal of corrosion products on gilded copper alloy artifacts*, **Current Problems in the Conservation of Metal Antiquities**, (Editor: A. Shigeo), Tokyo, 1993, pp. 215-224.
[36] I. Montero, S. Rovira, G. Delibes, J. Fernández-Manzano, M. Fernández-Posse, C. Herrán JI, Martín, R. Maicas, *High leaded bronze in the late bronze age metallurgy of the Iberian Peninsula*, **Archaeometallurgy in Europe**, **2**, 2003, pp. 3:1-8.
[37] V.K. Gouda, G.I. Youssef, N.A. Abdel Ghany, *Characterization of Egyptian bronze archaeological artifacts*, **Surface and Interface Analysis**, **44**(10), 2012, pp. 1338–1345.
[38] M. Quaranta, E. Catelli, S. Prati, G. Sciutto, R. Mazzeo, *Chinese archaeological artefacts: Microstructure and corrosion behaviour of high-leaded bronzes*, **Journal of Cultural Heritage**, **15**, 2014, pp. 283–291.
[39] D.A. Scott, **Metallography and Microstructure of Ancient and Historic Metals**, J. Paul Getty Museum, The Getty Conservation Institute, Los Angeles, 1991.
[40] W.T. Chase, *Chinese bronzes: casting, finishing, patination and corrosion*, **Ancient and Historic Metals**, (Editors: D.A. Scott, J. Podany and B. Considine), The Getty Conservation Institute, Los Angeles ,1994.
[41] I.G. Sandu, F.-A. Tencariu, D.-M. Vornicu, A.V. Sandu, A. Vornicu, V. Vasilache, I. Sandu, *Establishing the Archaeo-Metallurgic Ornamentation Process of an Axe from the Bronze Age by OM, SEM-EDX, and Micro-FTIR*, **Microscopy Research and Technique, 77**, 2014, pp. 918–927.

[42] V. Vasilache, D. Diaconu, O. Mircea, A. Drob, I. Sandu, *The Archaeometallurgical Evaluation of Three Bronze Socketed Axes, Discovered in Eastern Romania*, **Applied Sciences-Basel, 11**, 2021, Article Number: 1811. https://doi.org/10.3390/app11041811.
[43] I.G. Sandu, V. Vasilache, I. Sandu, F.A. Tencariu, A.V. Sandu, *Study on the Middle Bronze Age Disc-Butted Axe Ornament from Archaeometallurgical Point of View*, **Applied Sciences-Basel, 11, 2021,** Article Number: 9814. https://doi.org/10.3390/app11219814.
[44] I. Sandu, N. Ursulescu, I.G. Sandu, O. Bounegru, I.C.A. Sandu, A. Alexandru, *Pedological stratification effect of corrosion and contamination products on Byzantine bronze artefacts,* **Corrosion Engineering Science and Technology, 43,** 2008, pp. 256–266. https://doi.org/10.1179/174327807X234688.
[45] M. Ghoniem, *The characterization of a corroded Egyptian bronze statue and a study of the degradation phenomena*, **International Journal of Conservation Science**, **2**, 2011, pp. 95–108.
[46] M. Ghoniem, *Characterization and scientific conservation of a group of archaeological bronze Egyptian statues*, **International Journal of Conservation Science**, **7**, 2016, pp. 459-476.
[47] J. Ogden, *Metal*, **Ancient Egyptian Materials and Technology**, (Editors: P.T. Nicholson and I. Shaw), Cambridge University Press, Cambridge, 2000.
[48] D.A. Scott, L.S. Dodd, *Examination, conservation and analysis of a gilded Egyptian bronze Osiris,* **Journal of Cultural Heritage**, **3**, 2002, pp. 333–345.
[49] M. Ghoneim, *An Egyptian partially gilded bronze group statue: examination and analysis*, **Archaeometry**, **57**, 2015, pp. 130–146.
[50] L. Selwyn, **Metals and Corrosion: A Handbook for Conservation Professional**, Canadian Conservation Institute, Ottawa, 2004.
[51] I.G. Sandu, S. Stoleriu, I. Sandu, M. Brebu, A.V. Sandu, *Authentication of ancient bronze coins by the study of the archeological patina-I. Composition and structure,* **Revista de Chimie, 56**, 2005, pp. 981–994.
[52] I. Sandu, O. Mircea, A.V. Sandu, V. Vasilache, I.G. Sandu, *Study of the Liesegang Chemical Effects in Antique Bronze Artefacts During Their Stay Within an Archaeological Site*, **Revista de Chimie, 65**, 2014, pp. 311–319.
[53] D.A. Scott, *A review of copper chlorides and related salts in bronze corrosion and as painting pigments*, **Studies in Conservation**, **45**, 2000, pp. 39-53.
[54] S. Ahmed, M. Abdelbar, W. Sabry, A. Ali, *Experimental Study of Gap-Filling of Ancient Completely Corroded Copper Bowl Via Nano- Polymers*, **International Journal of Conservation Science**, **11**, 2020, pp. 97-108.
[55] M.F. Alberghina, R. Barraco, M. Brai, T. Schillaci, L. Tranchina, *Integrated analytical methodologies for the study of corrosion process in archaeological bronzes*, **Spectrochimica Acta**, **66**, 2011, pp. 129-137.
[56] A.A. Nofal, A.M. Waly, *Foundary technology of Ancient Egypt*, **Proceeding of the First International Conference on Ancient Egyptian Mining, Metallurgy and Conservation of Metallic Artifacts**, (Editor: FA. Esmael), Ministry of Culture, Supreme Council of Antiquities, Cairo, 1995, p. 178.
[57] * * *, https://permalac.com/ (accessed September 10, 2020)
[58] C. Sease, **A Conservation Manual for the Field Archaeologist**, Institute of Archaeology, University of California, Los Angeles, 1994.

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