Fayoum University

Faculty of Archaeology

Technical Investigation and Conservation of Core Cast Bronze Statuettes of Osiris

Mohamed Abdelbar
Faculty of Archaeology, Damietta University,
Egypt
ma00@du.edu.eg

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ABSTRACT

This study focuses on six Egyptian bronze statuettes dating from the Late Period (664-332 BC, which were cast around a sandy clay core using the lost-wax process. Theses statuettes depict the god Osiris and were excavated from Ehnasya, Beni Suef governorate, Egypt. They are distinguished by having thin walls, estimated to be approximately 1-1.5 mm thick. The analytical study aims to identify the metallic structure, corrosion crusts, casting core, and characterize the manufacturing technique. Various methods, including optical microscopy (OM), metallographic microscope, scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS), X-ray diffraction (XRD), and portable X-ray fluorescence spectrometer (pXRF), were employed. The results indicate that the statuettes were most likely made of leaded bronze alloy using the direct lost-wax method, a technique commonly used for manufacturing thin-walled bronze castings. The statuettes exhibit cracks and breaks in various areas, likely attributed to factors such as manufacturing defects, core expansion, or corrosion during burial. Corrosion products identified by XRD include clinoatacamite, cuprite, chalcopyrite, and those resulting from soil burial (calcite and quartz). The core is composed of a mixture of quartz and clay minerals. Finally, the statuettes underwent mechanical cleaning and treated with 3% (w/v) benzotriazole in alcohol, followed by the application of two layers of 3% (w/v) paraloid B-72 in acetone to insure long-term corrosion protection.

INTRODUCTION:

Thin-walled bronze statuettes were prevalent during the Third Intermediate Period (Circa 1070 – 664 BC) in Egypt, with further thinning observed in the Late Period (Circa 664-332 BC), making them susceptible to cracking, especially if the bronze wall thickness was one millimeter or less (Ogden 2000) (Mattusch 1996). Cracks and breaks in such statuettes may result from post-burial corrosion or interior core expansion during manufacturing (Garland 1927). The core's moisture retention and air bubbles in the molten bronze can induce internal stresses (Ogden 2000). Solid castings often underwent extensive engraving for fine details, while thin-walled statuettes, due to their delicate nature, could not withstand such mechanical work. So, it would have been common sense to include as much fine detail as possible in the original wax model (Ogden 2000) (Garland 1927).

Bronze's excellent casting qualities have led to the development of techniques like the lost wax method and the construction of complex molds (Forbes 1964) (Petrie 1996) (Hodges 1964). This process, originating in the third millennium BC in the Middle East and later spreading to Egypt, was crucial for reproducing intricate details and crafting thin-walled statuettes (Noble 1975) (Garland 1927). From the Late Period (664-332 BC) to the Graeco-Roman era (332 BC - 395 AD) in Egypt, lost-wax casting saw mass production of deity figures. Bronze figurines served as expressions of devotion and were often donated to temples as votive offerings (Scheel 1989). The expansion of industry during the Late Period resulted in the production of substantial quantities of low-quality statuettes for temple offerings (Ogden 2000).

The lost-wax technique encompasses two main methods: direct and indirect. In direct lost-wax casting, a clay or sand core resembling the actual statue's size and shape is created. Wax is then modeled over the core, with its thickness matching the required metal thickness (Petrie 1996). Metal rods or wires are inserted through the wax into the mold to secure the core while the wax is melted out (Mattusch 1996). Runners for pouring in metal and risers for releasing gases are usually attached to the wax model (Reedy 1991). The wax model is coated with clay, followed by heating to harden the clay mold and remove the wax, creating space for the molten metal to be cast. Finally, the mold is broken to access the casting, rendering it unusable, although the core may sometimes remain (Scheel 1989). Some cores inside animal figurines were intentionally removed after casting to insert a mummified animal (Garland 1927) (Hodges 1964) (Hodges 1970) (Hunt 1980).

The indirect process minimizes the risk of damaging the original model, allowing bronze founders to produce multiple wax models from a single master model (Mattusch 1996) (Oron 2006). This method involves creating molds for each part of the model, later assembling them (Michalopoulou 2017). The inner mold surfaces are coated with wax, followed by pouring clay inside. After disassembling the molds, additional details are manually added to the wax model (Hunt 1980) (Michalopoulou 2017). This secondary model, termed the 'inter-model,' is then invested and cast similarly to the direct process (Oron 2006).

For metal founders, hollow casting offers advantages over solid casting, as it is more economical in terms of wax and metal usage for core casting. Thinner walls are preferred to control distortion or shrinkage during solidification of large volumes of metal (Scheel 1989) (Oron 2006) (Cavanagh 1990) (Castelle 2016). Failures and defects in casting hollow figurines with the lost-wax process can occur due to impurities in the metal or uneven temperatures during casting (Gravett 2011). The molten bronze's exact temperature depends on the alloy and the metal wall's relative thickness. Thinner walls require higher molten metal temperatures to ensure complete cavity filling (Cavanagh 1990). Occasionally, chaplets failed to securely hold the core, resulting in unevenly thin casting walls. In cases of small casting failures, it was often more cost-effective to abandon the piece and start anew (Noble 1975).

Bronze artifacts recovered from burial environments are often covered by a dense layer of soil minerals associated with corrosion products. The degradation processes of thin-walled bronze statuettes during long-term burial in the soil are affected by several factors, including the object itself and soil properties. Other factors that can damage objects with thin walls include static and dynamic pressures in the soil (Robbiola 1997) (Gerwin 2000) (Nord 2005) (Selwyn 2006) (Oudbashi 2018) (Ingo 2019). After excavation, if copper chlorides are present, improper storage conditions could induce a cyclic and selfsustaining deterioration phenomenon commonly known as "bronze disease" (Mezzi, de Caro, et al. 2012) (Casaletto 2017). The current study aims to investigate a group of thin-walled bronze statuettes of Osiris dating back to the Late Period. To achieve this goal, various analytical methods were employed, including visual investigation, digital light microscopy, metallographic microscopy, portable XRF, XRD, and SEM/EDS. Finally, restoration and conservation procedures were performed to reveal the original surface and to provide reliable long-term protection.

1. MATERIALS AND METHODS

1.1 Statuettes descriptions

The research centers on six statuettes from the Late Period, currently preserved in the store museum of Kom Oshim, Fayoum, Egypt, with catalog numbers 8/26 to 13/26. These statuettes were discovered at Ehnasya in the Beni Suef Governorate, Egypt, by chance in 1956 and have remained without any conservation processes (Figs. 1 and 2). The statuettes depict the Egyptian God Osiris in human form, characterized by curved beards, with one of them seated and the others in standing positions. They are depicted in mummy wrappings, wearing a distinctive crown adorned with two large ostrich feathers on either side and holding a symbolic crook and flail. The seated statuette (No.8/26) measures 15.6 cm in height and weighs 134 grams. This statuette is relatively rare compared to the standing Osiris (No.9/26), which is 12.3 cm tall and weighs 107 grams. The remaining figurines, identified as numbers 10/26, 11/26, 12/26, and 13/26, vary in height from 9.8 cm to 11.9 cm and weigh between 52 grams and 68 grams.

1.2 Technical investigation

In-situ, a handheld digital microscope (Rohs USB) with magnifications of 50x and 500x was utilized to study the patina morphology. Broken statuettes provided opportunities to inspect and sample the interior core in areas where the metal had been lost, facilitating investigations into metal wall thickness. A cross-section sample was prepared to study the alloy microstructure and corrosion conditions. Initially, it was polished using silicon carbide abrasive paper and further polished with a ½ µm alumina suspension. Special care was taken during the preparation of metallographic sections of leaded alloy samples to prevent the loss of lead globules during grinding and polishing. If they do fall out, they leave small spherical holes, and it may then become very difficult to distinguish between porosity due to casting defects and lead globules as an alloying component, both appearing as holes in the polished section (Scott 1991). The metallurgical features were studied using a Leco L31 metallographic microscope to identify the alloy's microstructure. Micrographs were captured on an unetched, polished surface, followed by etching with an alcoholic ferric chloride solution (240 mL ethanol, 60 mL hydrochloric acid, and 20 g ferric chloride) for five seconds. The cross-section sample was initially examined with the Inspect S50 Scanning Electron Microscope (SEM), FEI company, with energy dispersive spectroscopy (EDS) to determine the surface composition and its microstructure. Non-destructive analysis was performed using a portable X-ray Fluorescence (XRF) analyzer, Bruker S1 TITAN and TRACER 5i (Germany), to identify the metallic components of the manufacturing alloy. The analysis was conducted at a voltage of 40 kV, a current of 40 uA, an acquisition time of 40 s, and a collimator of 3 mm. Two samples of corrosion products and one sample of the casting core were analyzed by X-ray diffraction (XRD) using the Empyrean series 3 X-ray diffraction with a Cu-target tube at 60 kV and 60 mA.

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Fig. 1. Seated and standing bronze statuettes of Osiris, the patina is covered by a thick layer of soil deposits. The lower legs of no. 9/26 had completely lost. Front views.

Fig. 2. Back views of the statuettes show the metal body is cracked and disrupted, missing areas could be seen in the legs and the crown.

1.3 Conservation procedures

Conservation treatments were mechanically carried out to remove soil encrustations and corrosion products, thus revealing the original surface and restoring the complete legibility of the statuettes. The interventions involved the use of hand tools such as scalpels, scrapers, dental picks, and soft-bristle brushes. Following this cleaning process, the statuettes were brushed with two layers of 3% (w/v) benzotriazole (BTA) in ethanol. Excess BTA was removed using a cloth saturated with ethanol. Finally, two layers of 3% (w/v) Paraloid B72 in acetone were applied to the statuettes. Subsequently, the statuettes were individually packed in polyethylene boxes containing silica gel to maintain appropriate temperature and relative humidity until transportation to a controlled environment.

2. RESULTS AND DISCUSSION

2.1 Visual and microscopic examination

In the seated statuette (No.8/26), a severe crack measuring approximately 1.5 mm in width is evident in the head, and a missing area is observed at the top of the crown (see Fig. 3). Additionally, in Fig. 4, cracks are found in the mass of the right feather, indicating that these cracks occurred after manufacturing and the solidification of the molten metal. Macro cracks extending from the knees to the feet, ending with a missing part, are also noticeable. Typically, seated statues had a tang underneath the buttocks and another underneath the feet to secure the statue to a base made of metal or wood, but these tangs are missing, as illustrated in Fig. 5. In the standing statuette (No. 9/26), there is a substantial missing part in the entire lower legs, as shown in Fig. 6. Cracks and breaks are also observed in the legs and the crown of the four figurines (10/26 to 13/26), as depicted in Fig. 7 and 8. Statuette No. 10/26 is almost entirely mineralized, with only small remnants of metal on the upper part. A large gap in the knees at the back, with a width of 4 cm, poses a risk of breaking the statuette in half, as shown in Fig. 9. The thickness of the metal wall was measured in situ, as shown in Fig. 10a, and through cross-section SEM examination, as marked in Fig. 10b.

Due to the statuettes being buried in the soil for an extended period, their surfaces were covered with thick layers of soil minerals and straw, concealing their features and details. Simple cleaning revealed that all statuettes appeared to have the remaining metallic core preserved within the corrosion products and soil encrustations. One figurine, number 10/26, had completely transformed into corrosion products. The small weight of the statuettes indicates a thin bronze wall thickness, ranging from 1 to 1.5 mm. This suggests that they were made using the direct lost-wax technique rather than the indirect method. The direct lost-wax method was employed to achieve thinner walls, eliminating potential casting defects associated with the indirect lost-wax technique. The latter technique typically required a minimum wall thickness of approximately 3 mm (Mille 2017). Castings produced via the indirect process tended to exhibit more uniform metal thickness compared to those made using the direct method (McArthur 2015).
Microscopically, the casting cores displayed incoherence, numerous pores, and cracks, as shown in Fig. (5,f - 6,c - 7,e - 8,b - 9,e). During casting, the porosity of the core facilitated the escape of gasses when the molten metal was poured (Reedy 1991). The degradation of the casting cores was a result of the deterioration process over time in the soil. The core material appears black, consistent with the typical appearance of other statuettes. Blackened cores resulted from the burning of organic matter and any absorbed waxes or resins during casting. Other core materials included gypsum and calcium carbonate (Ogden 2000).

At the broken top of the crown of the seated statuette, it appeared that the white core material could be attributed to gypsum residue used for investment, as shown Fig. 3e. Cross-section investigations revealed that the original metal of the wall was preserved within a sandwich corrosion crust. Green and blue corrosion products were observed at the interface between the inner core and the metal body, as identified in Fig. 6b. The metal wall had completely transformed into light green copper trihydroxy chlorides, as shown Fig. 9d. SEM examination estimated the thickness of the metal wall to be approximately 1.3 mm, as marked in Fig. 10b.

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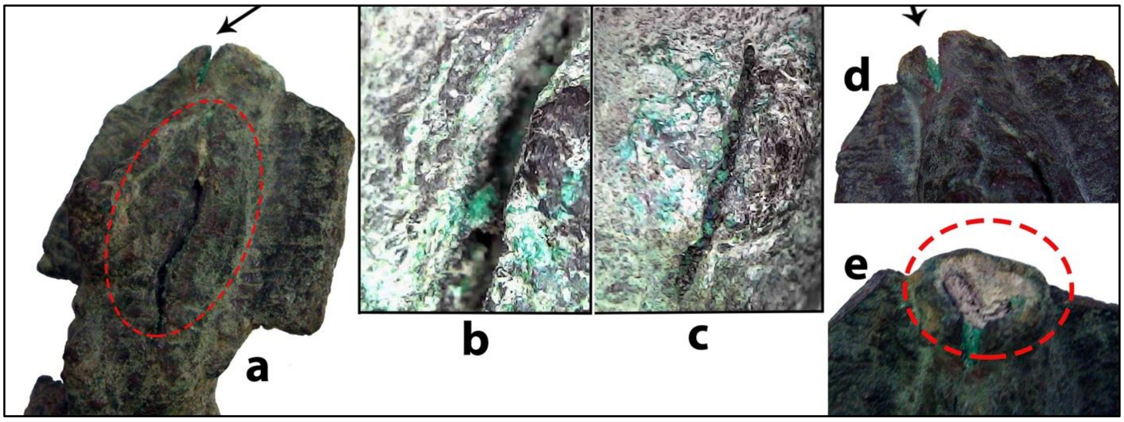

Fig. 3. (a,d). Cracks appear in the head. (e). Missing area could be seen in the crown. (b,c). USB microscopic images show cracks in the head.

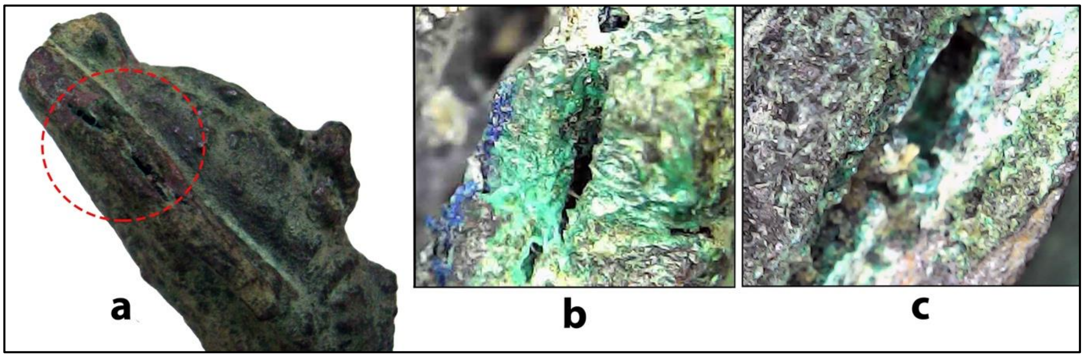

Fig. 4. (a). Cracks are found in the mass of the right feather; (b,c). Images with a USB microscope show the cracks.

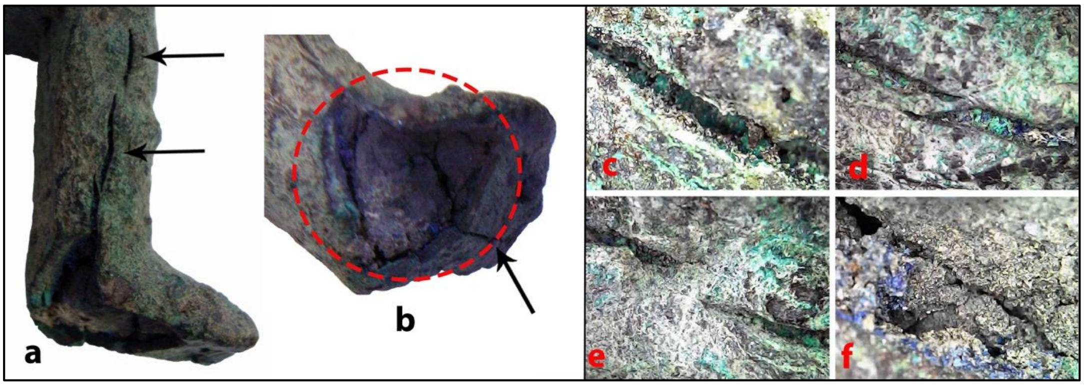

Fig. 5. (a,b) Cracks and missing areas is observed in the leg. (c-e) Images with a USB microscope show cracks in the legs. (f) Blue corrosion products and cracks could be seen in the casting core.

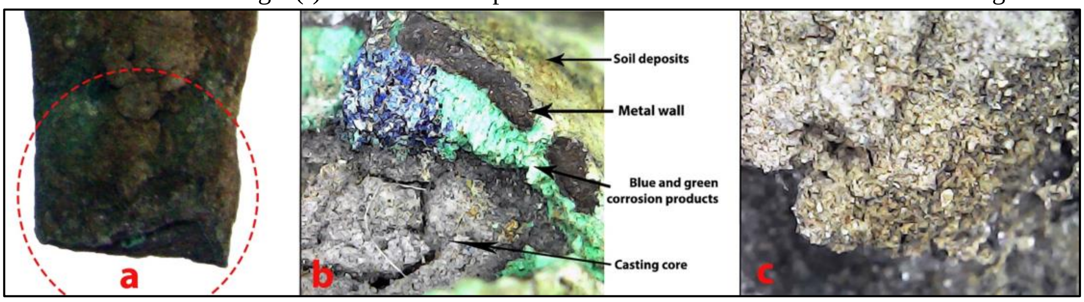

Fig. 6. (a) The entire lower legs were missed. (b) Cross-section shows copper trihydroxychlorides located in the inner surface between the metal wall and the core. (c) The casting core is fragile and cracked.

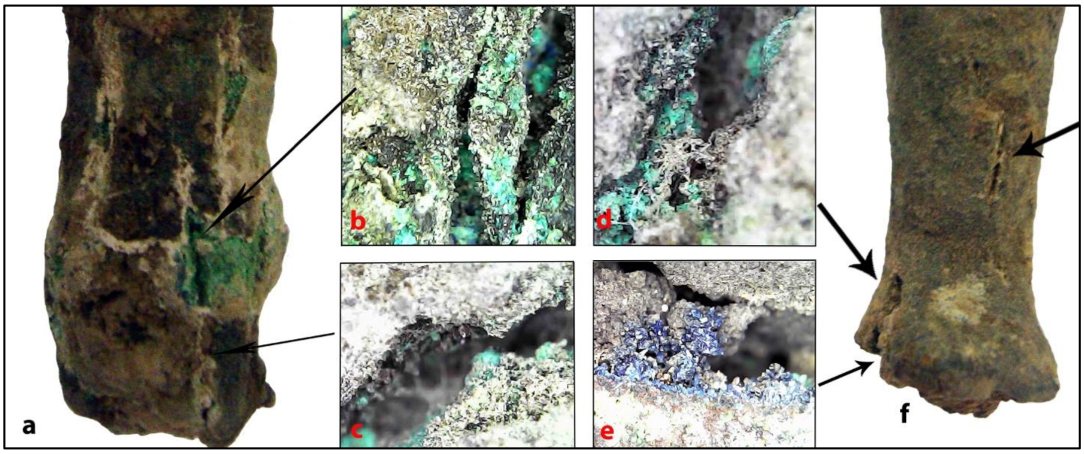

Fig. 7. (a,b,c,d,f) Cracks are found in the metal wall. (e) Blue corrosion products were associated with the casting core.

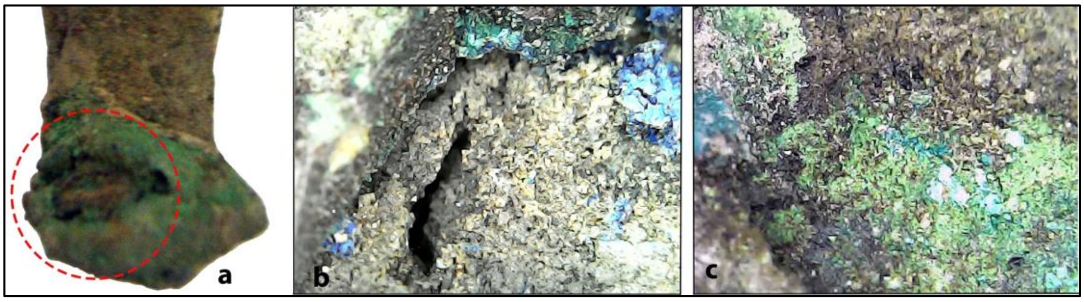

Fig. 8. (a) Missing area is observed in the feet. (b) The casting core was cracked. (c) The patina is incorporated with soil minerals.

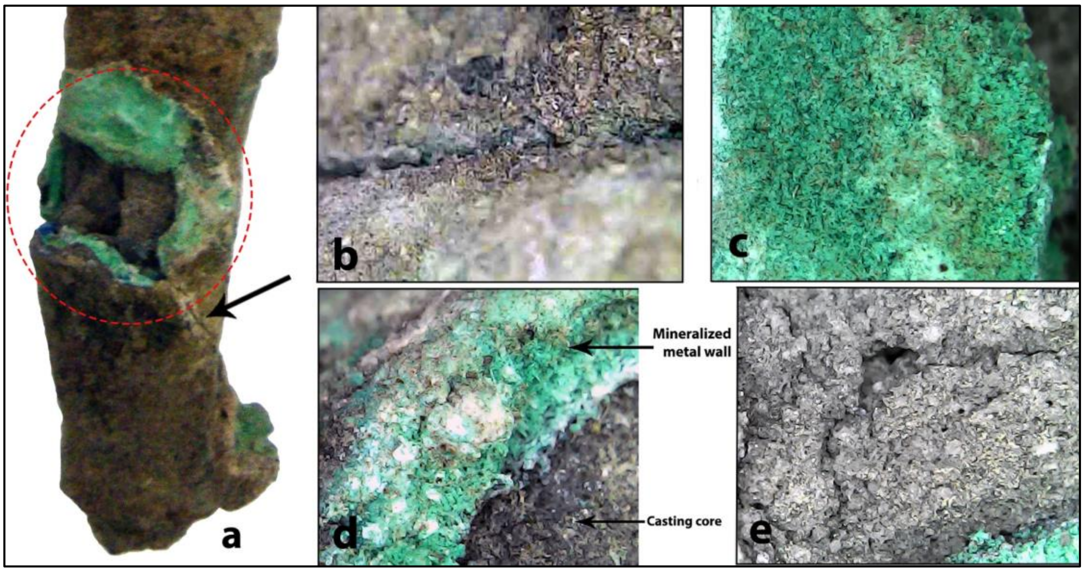

Fig. 9. (a, b) Large gap and cracks appear in the legs from behind. (c) Trihydroxychlorides could be seen in contact with the casting core. (d) Cross-section shows the metal wall had completely transformed to chloride compounds. (e) The casting core is full of cracks and pores.

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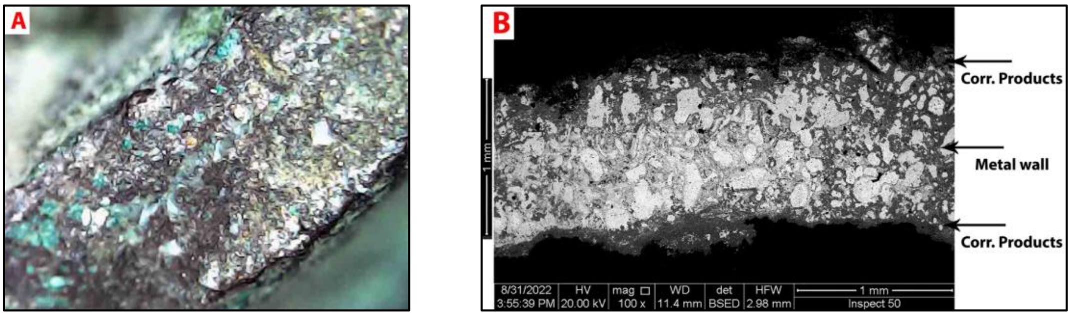

Fig. 10. (a) In Situ USB microscopic image of the metal wall after mechanical cleaning. (b) SEM examination of cross-section shows the metal wall thickness is measuring approximately 1.3 mm.

2.2 Alloy microstructure

Metallographic and scanning electron microscope examinations of the alloy cross-section were conducted in both unetched and etched conditions, as depicted in Fig. 11. The matrix consists of the primary α-Cu phase (light colored), Cu–Sn intermetallic compound (dark colored), and lead particles (black colored) as illustrated in Fig. 11a and b (Scott 1990) (Silva 2008) (Gupta 2016). The metallographic images reveal that lead particles are coarse, indicative of a very slow solidification rate (Gouda 2012). Lead has limited miscibility in copper in the liquid state and is virtually insoluble in the solid state (Robbiola 1997). It forms small globules and is well distributed in low-lead bronzes or large, irregular globules in highly leaded bronzes. Alloys containing a high percentage of lead have been used to cast objects that likely have thin walls (for rapid solidification) and do not require good physical properties, such as high tensile strength. In lower proportions, lead negatively affects the physical properties of the final casting, but also makes the melt less viscous and facilitates casting (Chase 1994). SEM examination confirmed that the large and irregularly distributed globules in the bronze matrix are from Pb rich microconstituent, as shown in Fig. 11c.

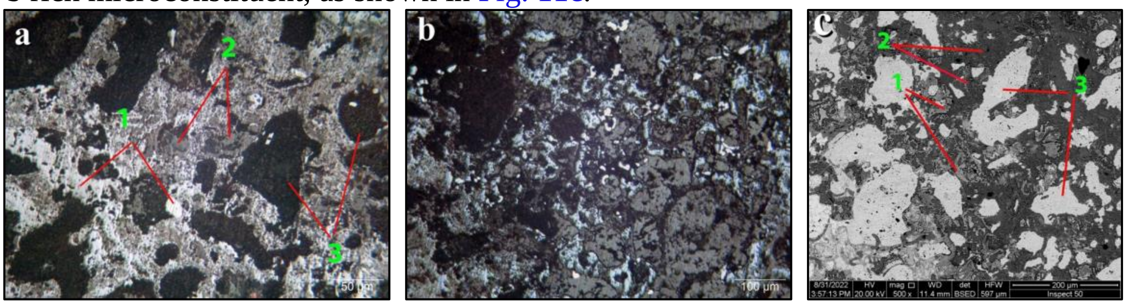

Fig. 11. Metallographic images show the microstructure of leaded bronze. **1**) α-Cu phase, **2**) Cu–Sn intermetallic, and **3**) large and irregular globules of lead. **a** (unetched), **b** (etched), **c** (SEM micrograph).

2.3 Elemental composition of the alloy

Surface analysis was conducted at three spots on each statuette using portable XRF, and the averaged results are presented in Table 1. Additionally, SEM/EDX analysis was performed on a polished cross-section sample, as shown in Fig. 12 and

Table **2**. XRF measurements indicated that the alloy of the statuettes consisted of leaded bronze with approximately 2.82 wt% tin and 13.04 wt% lead. Early craftsmen chose to incorporate tin and lead with copper based on availability and the desired physical properties of the bronze. Tin serves to harden copper, while lead lowers the melting point. During the Late Period, ancient Egyptians used highly leaded bronzes for crafting statuary and intricate ornaments. The presence of approximately 13% lead significantly increases the fluidity of molten bronze, making it easier to cast thinner walls (Ogden 2000) (Cavanagh 1990) (Chase 1994). The soil crusts identified in the analysis contain high amounts of Si, Al, Ca, and Fe, and lower amounts of P, characteristic of clayey sand soil (Robbiola 1997). The chloride content varies from 1.479% to 11.582%, indicating the presence of chloride compounds in the patina. This suggests that the soil contains high levels of chloride ions (Oudbashi 2018). Notably, statuette No. 10/26 exhibited the highest chlorine content, having been completely transformed into chloride products.

The elementary composition was confirmed through SEM/EDX analysis on a polished cross-section, verifying that the statuettes are made of a leaded bronze alloy. EDS analysis conducted on white globules revealed them to be Pb-rich metallic compounds containing approximately 96.84 wt% lead. The presence of some copper (3.16%) in the composition of these inclusions might be attributed to the surrounding bronze matrix in the EDS microanalysis. Representative EDS maps of Cu, Sn, Pb, and Cl are provided in Fig. 13, illustrating the distribution of these elements within the alloy structure.

Table 1. XRF results show the chemical composition of the bronze surface (wt.%).

Statuette	Alloy elements (Wt. %)			Soil elements (Wt. %)					
	Cu	Sn	Pb	Fe	Al	Si	P	Cl	Ca
(8/26)	78.373	3.146	12.917	0.760	0.549	1.955	0.171	1.730	0.399
(9/26)	76.914	3.141	13.477	0.679	2.196	1.562	0.125	1.246	0.660
(10/26)	64.813	2.942	12.504	0.833	1.325	4.099	0.189	11.582	1.713
(11/26)	72.069	2.713	12.801	1.294	2.899	3.641	0.029	2.348	2.206
(12/26)	67.077	2.953	13.925	0.784	3.313	4.134	0.256	4.745	2.813
(13/26)	73.120	2.951	13.700	0.528	2.985	2.223	0.109	1.479	1.905

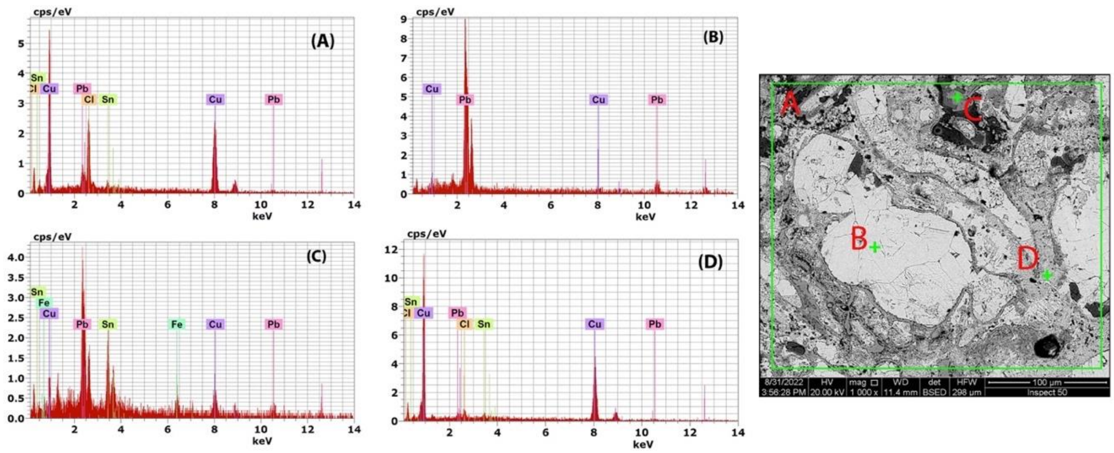

Fig. 12. SEM images and EDS spectra show microstructural features of the bronze surface.

Table 2. EDS analysis shows results illustrating the phases in the alloy.

Element wt% / Spot	Cu	Sn	Pb	Cl	Fe
A	79.61	2.81	9.57	8.01	---
B	3.16	---	96.84	---	---
C	23.66	28.81	45.80	---	1.73

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D	87.34	4.55	7.03	1.08	---

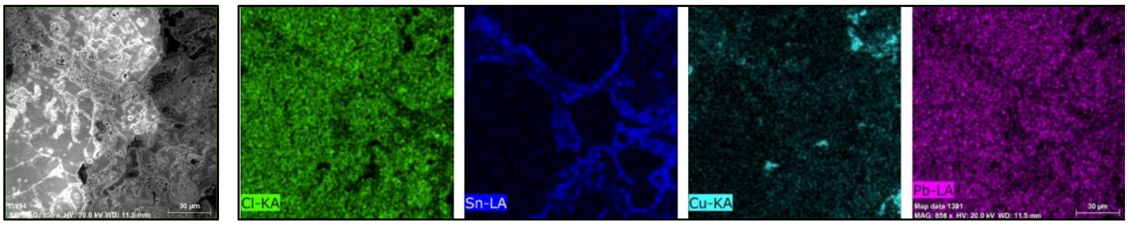

Fig. 13. EDS elemental maps of a cross-section of the bronze alloy show the distribution of Cu, Sn, Cl, and Pb.

2.4 Characterization of the inner mold (the core)

Various core materials were historically used in lost-wax casting, with mixtures of fine clay and charcoal dust being common. In ancient Egypt, the casting cores for hollow bronze objects were typically made from sandy clays combined with organic binders such as dung, chaff, or carbon derived from bone or sawdust. This choice was based on their ability to penetrate through holes in the mold material after burning (Ogden 2000) (Nofal 1995). Fine clays were not preferred because clay cores didn't require specific color or unique properties like plasticity or strength (Reedy 1991). One sample of the casting core was subjected to XRD analysis, and the results presented in Fig. 14 and Table **3**. The analysis revealed that the material used for the inner core consisted of a mixture of quartz and clay minerals (microcline, albite, and anorthite) in a 1:1 ratio. Mixtures of clays and sands have a long history in the production of hollow-cast bronze statues (Castelle 2016). Sand is advantageous as an ingredient because it increases the fired clay's capacity to withstand high casting temperatures, preventing shrinking and cracking of the core. It also helps prevent casting flaws by increasing core porosity, providing escape routes for expanding gasses during metal pouring (Reedy 1991) (Gettens 1969). Feroxhyte, an iron compound, was detected in the XRD analysis of the casting core. This compound is found in the core material of a statuette from the same period may have originated from the surrounding burial environment or the core material itself (Abdelbar 2021). It is evident that some means of supporting the core during casting were necessary, and iron rods or wires (armatures) might have been used for this purpose (Reedy 1991). These wires would oxidize completely in the black core material and scatter somewhat among it, making them difficult to detect. However, it is unlikely that the ancient Egyptians used bronze supports because of their relatively small size, and molten metal would likely melt them during pouring (Garland 1927).

2.5 The Degradation processes

The six statuettes were buried in moist soil rich in oxygen, sulfur, and chloride. Their surfaces were entirely covered with green-colored corrosion products, with a few blue corrosion products presents. The outer corrosion layer included soil minerals associated with organic residues. Two samples of corrosion products were subjected to XRD analysis, and the results are presented in Fig. 15,16, and

Table **3**. The first sample, consisting of corrosion products mixed with soil particles, comprised cuprite, clinoatacamite, chalcopyrite, quartz and calcite as soil products. The second sample, from statuette no. 10/26, was completely mineralized and primarily composed of clinoatacamite with a small amount of cuprite. The results confirmed that the patina consisted of cuprite (Cu_2O), clinoatacamite ($Cu_2(OH)_3Cl$), and chalcopyrite ($CuFeS_2$), covered with thick layers of soil deposits. Cuprite is the layer overlying the original metallic surface in many bronzes during burial. Copper chlorides can transform a solid bronze object into light green powders under harsh conditions (Scott 2000) (Scott 2002). Four phases of copper trihydroxychlorides of with the same chemical formula $Cu_2(OH)_3Cl$ (clinoatacamite, atacamite, paratacamite, and botallackite) can form, each with different crystal structures (Pollard, Williams and Thommas 1989) (Scott 2000). These compounds result from the hydrolysis of cuprous chloride (nantokite) of composition CuCl when ample oxygen and water are present, reacting very quickly to give the basic copper(II) chloride, paratacamite, amongst other products. ($CuCl_2.3Cu(OH)_2$) (Fischer 1997). Paratacamite often appears as a powdery, light green secondary corrosion layer on the patina surface or in active corrosion blisters. Clinoatacamite replaced paratacamite in natural occurrences because paratacamite is stabilized by small amounts of zinc or nickel impurities, while clinoatacamite exists without these impurities. There is a strong similarity between X-ray diffraction data for paratacamite, atacamite, and clinoatacamite, whilst botallackite is the least stable of them. In this context, due to the absence of zinc in the alloy composition and X-ray powder patterns (d-spacings and relative intensity), the presence of clinoatacamite is more likely than paratacamite (Scott 2000) (Selwyn 2004) (Scott 2016). The formation of copper iron sulfide, chalcopyrite ($CuFeS_2$), on buried bronze statuettes could be attributed to soil rich in oxidized organic matter and sulfate-reducing bacteria (SRB) thriving in anaerobic environments (Scott 2002). These bacteria convert sulfate species into sulfide through a process known as microbial corrosion. The presence of Fe^{3+} ions in the sulfide corrosion product is related to the presence of iron-containing compounds in the surrounding environment (Ingo 2019). Quartz and calcite, detected in the XRD analysis of the corrosion samples, are indicative of soil minerals originating from the burial environment.

The six studied statuettes have experienced cracking, loss, and breakage. The reasons for these phenomena in thin-walled castings can be attributed to three possible scenarios:

- Manufacturing defects: These can occur if air bubbles form in the molten bronze during casting, causing the core to expand and create internal pressures leading to cracks (Ogden 2000). Temperature control during casting is crucial, as inadequate temperature can result in incomplete mold filling. Improperly positioned cores within the mold can also lead to uneven wall thickness and subsequent cracking (Cavanagh 1990) (Noble 1975).
- Chemical composition and metallurgical characteristics of the alloy: The presence of lead in the alloy plays a significant role in the corrosion mechanism. During alloy solidification, intergranular corrosion tends to occur, leading to increased corrosion during burial. (Sandu 2005).
- Degradation processes during long-term burial: The weight of the soil, particularly in thin-walled statues, can produce high stresses. The internal core (sandy clay) expands due to water absorption, and copper trihydroxy chlorides, especially in the interface between the core and the metal wall, increase in volume. Both factors contribute to physical stress within thin-walled metal objects, resulting in cracking or fragmentation (Garland 1927) (Scott 2002).

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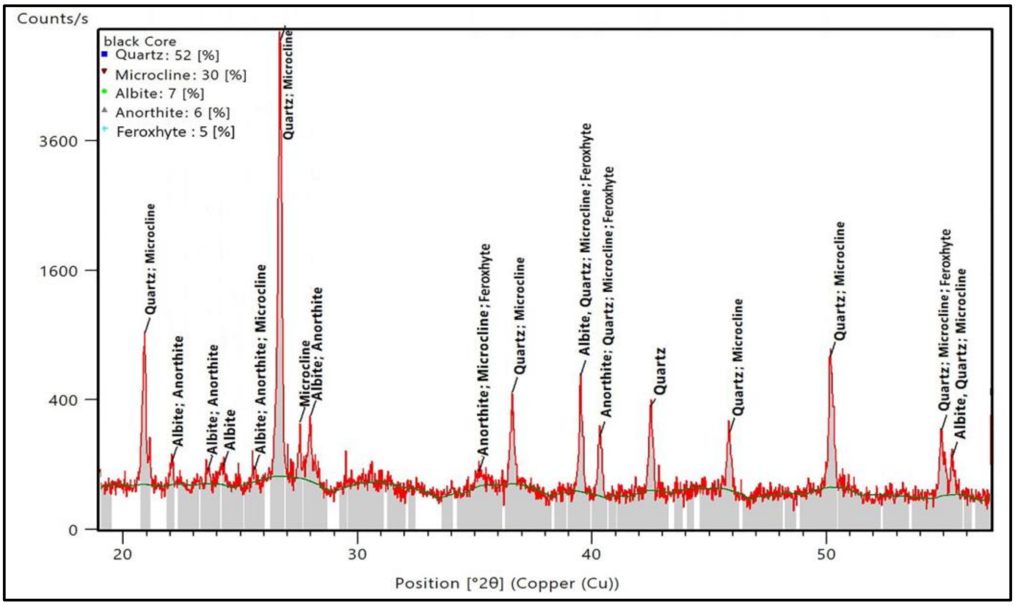

Fig. 14. XRD pattern shows the composition of the casting core.

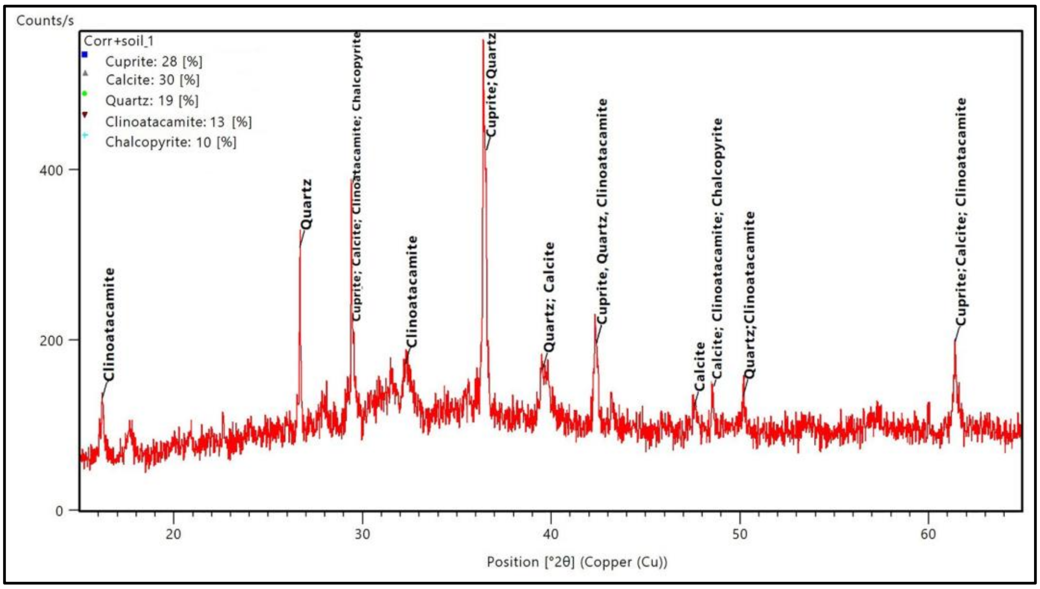

Fig. 15. XRD pattern shows corrosion products covered by soil deposits.

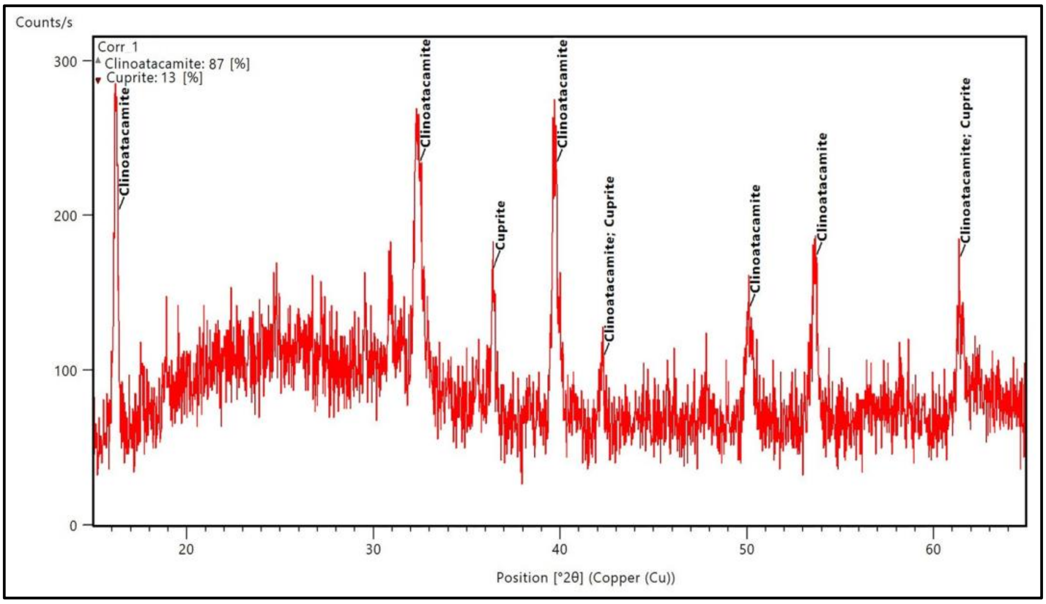

Fig. 16. XRD pattern of trihydroxychloride as a major corrosion product.

Table 3. XRD results show the corrosion products, soil minerals, and the casting core.

Sample	Crystalline Component	Compound Name	Chemical Formula	Ref.Code	Semi-quantitative
Corrosion products with soil	Cuprite	Copper Oxide	Cu_2O	01-075-4299	28 %
	Clinoatacamite	Copper Hydroxide Chloride	$Cu_2(OH)_3Cl$	01-078-7708	13%
	Chalcopyrite	Copper Iron Sulfide	$CuFeS_2$	01-086-4137	10%
	Calcite	Calcium Carbonate	$CaCO_3$	01-075-6049	30%
	Quartz	Silicon Oxide	SiO_2	01-079-6238	19%
Light green corrosion products	Clinoatacamite	Copper Chloride Hydroxide	$Cu_2(OH)_3CI$	01-078-7708	87%
	Cuprite	Copper Oxide	Cu_2O	01-075-4299	13%
Casting Core	Quartz	Silicon Oxide	SiO_2	01-079-6238	52%
	Microcline	Potassium Aluminum Silicate	$KAlSi_3O_8$	01-071-0955	30%
	Albite	Sodium Calcium Aluminum Silicate	$(Na,Ca)Al(Si,Al)_3O_8$	00-041-1480	7%
	Anorthite	Calcium Aluminum Silicate	$CaAl_2Si_2O_8$	00-041-1486	6%
	Feroxhyte	Iron Oxide Hydroxide	δ′-FeOOH	00-013-0087	5%

2.6 Conservation treatment

Metallic objects are typically cleaned mechanically and chemically to reveal the original metal surface while retaining the outer layer of green-colored corrosion products. It is generally advisable to clean only what is necessary to prevent potential damage to the object's shape during chemical treatment. Since the statuettes exhibited cracks and missing areas distributed throughout, chemical solutions could penetrate the inner core and potentially cause future damage. Therefore, mechanical cleaning was preferred in this

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case. During the cleaning process, removing soil or earthy minerals to expose the outermost layers of the bronze patina typically poses no significant challenges (Scott 2002). In the case of the studied statuettes, the dense layers of soil were mechanically removed using a sharp scalpels, scrapers, and dental picks under magnification, while leaving the layer of green-colored corrosion products intact, without exposing the cuprite layer. Preventing CuCl from reacting with post-excavation environments is crucial to avoid cyclical oxidation and hydrolysis mechanisms catalyzed by Cl^-. To address this, treatments included the mechanical removal of chloride compounds followed by inhibition with benzotriazole. Benzotriazole (BTA $C_6H_5N_3$) is known for its high effectiveness as a corrosion inhibitor for copper and its alloys. It forms very stable complexes, Cu(I)BTA and Cu(II)BTA, which act as passive layers, isolating the bronze object from oxygen and moisture (MacLeod 1987) (Mezzi, Angelini, et al. 2012). Once the mechanical cleaning was completed, the statuettes were brushed with two layers of 3% (w/v) benzotriazole (BTA) in ethanol. Excess BTA was removed using a cloth saturated with ethanol. Statuette No. 10/26, which was entirely mineralized, received treatment with a 30% by weight benzotriazole solution dissolved in ethanol to ensure adequate protection. It's worth noting that low concentrations of benzotriazole may not provide satisfactory protection for objects heavily attacked by chloride (Madsen 1971). Finally, two layers of 3% (w/v) Paraloid B-72 in acetone were applied to ensure future corrosion protection for the statuettes, especially when stored in uncontrolled environmental conditions, as depicted in Fig. 17. Once the conservation process was complete, the objects were wrapped in polyester sheets and placed in polyethylene-sealed containers with silica gel for optimal metal conservation.

Fig. 17. The Osiris bronze statuettes after conservation processes.

3. CONCLUSION

The data obtained from the study reveals that the six statuettes were crafted from a leaded bronze alloy, a traditional choice for manufacturing small figurines during the Late Period of Egypt. The average composition of the bronze is 2.82 wt% tin, 13.04 wt% lead, and the rest is copper find. SEM examinations provided valuable insights into the metal wall thickness, which was found to be approximately 1-1.3 mm. This information about wall thickness provides compelling evidence that the statuettes were cast using the direct lost-wax method rather than the indirect method. The casting core, made from a mixture of sand and clay, has become fragile and cracked over time due to prolonged burial in the soil. The presence of copper trihydroxy chloride (clinoatacamite), as identified by XRD, and the high chloride content detected by XRF indicate that the burial soil contained elevated levels of chloride ions. Based on these findings, it can be concluded that some cracks observed in the seated statuette occurred during casting, while in others, cracks and breaks resulted from degradation processes during burial. These cracks in the metal wall allowed the penetration of ions dissolved in the soil water into the interior of the statue, inducing corrosion from the inside and leading to the loss of metal in some areas. In the context of the conservation treatments applied, mechanical cleaning was deemed preferable to chemical cleaning. This choice was made to mitigate the risk of chemical solutions penetrating the inner core and causing potential damage in the future.

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الدراسة الفنية والصيانة لتماثيل برونزية لأوزوريس مصبوبة حول لب داخلي

محمد عبدالبر
كلية الاثار،
جامعة دمياط
ma00@du.edu.eg

الملخص

تتناول هذه الدراسة ستة تماثيل برونزية من العصر المتأخر (٦٦٤-٣٣٢ قبل الميلاد) مصنوعة بطريقة الصب حول حشو من الطين الرملي بطريقة الشمع المفقود. هذه التماثيل تمثل المعبود أوزوريس وقد تم الكشف عنها في مدينة إهناسيا بمحافظة بني سويف، مصر. تميزت هذه التماثيل بجدران برونزية رقيقة تقدر بحوالي ١-١,٥ مم. أجريت الدراسة التحليلية للتعرف على التركيب المعدني ونواتج الصدأ وحشو الصب وتحديد أسلوب الصب المستخدم. ولهذا الغرض، تم تطبيق طرق مختلفة، تتمثل في الفحص بالميكرسكوب الضوئي، الميكرسكوب الميتالوجرافي، الميكرسكوب الإلكتروني الماسح المزود بوحدة تحليل العناصر، حيود الأشعة السينية وتفلور الأشعة السينية المحمول. أوضحت النتائج أن التماثيل مصنوعة من سبيكة البرونز الرصاصي بأسلوب الصب المباشر بطريقة الشمع المفقود، حيث أستخدم هذا الأسلوب في صناعة التماثيل ذات السمك الرقيق. تعاني هذه التماثيل من وجود الشروخ في أماكن متفرقة، وقد تبين أن أسباب هذه الشروخ يرجع اما الى عيوب في التصنيع او نتيجة للتمدد الحادث للب الداخلي أو بفعل الصدأ أثناء الدفن في التربة. أظهرت دراسة نواتج الصدأ أنه تم تحديد مركب الكلينواتاكاميت والكوبريت والكالكوبيريت، بالإضافة الى تلك المركبات الناتجة عن الدفن في التربة (الكالسيت والكوارتز). وتظهر النتائج أن مادة الحشو الداخلي تتكون من خليط من معادن الكوارتز والطفلة. في النهاية الدراسة، تم تنظيف التماثيل بالطرق الميكانيكية ثم معالجتها بالبنزوتريازول الذائب في الكحول بتركيز ٣٪ (وزن / حجم). تم تطبيق طبقتين من البارالويد ب ٧٢ الذائب في الأستيون بتركيز ٣٪ (وزن / حجم) لتوفير حماية موثوقة طويلة الأجل من الصدأ.

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