A Scientific Study of Inlaid Iron Statuettes from 12th-16th Century AD

Assist. Prof. Dr. Abeer Gharib Abdallah
Head of conservation department, Faculty of Fine Arts, Minia University, 61519 Minia, Egypt.
abeer.ibrahim@mu.edu.eg

ABSTRACT

This paper aims at examining and analyzing Egyptian inlaid metallic statuettes from 12th-16th century AD. This inlaid statuettes exhibited in the museum of Faculty of Applied Arts in Cairo. Examination and analysis were performed using optical microscopy (OM), scanning electron microscopy coupled with energy dispersive x-ray spectrometry (SEM-EDX) and x-ray diffraction (XRD). The SEM-EDX examination showed that the bodies of two statuettes are made of cast iron alloy and inlaid with brass alloy, the brass strips were flaking and detachment. The XRD results revealed the dominant phases were goethite (α-FeO(OH)), akagantite and magnetite specially on the internal statuettes surfaces. The study allowed establishing the manufacture technology and its effect on chemical alteration and physical damage processes. This study may help to assessment and understand the corrosion process or corrosive environmental condition affected on the inlaid metallic statuettes.

Keywords
Cast Iron; Inlaid Statuettes; Corrosion; OM; SEM-EDX; XRD

1. INTRODUCTION

The analysis of metal objects leads to illustration of manufacturing and processing conditions employed by ancient craftspeople (Mircea et al., 2013; Valério et al., 2016). Metallic objects undergo physical-chemical transformations involving complex mechanisms, which modify both the metallic core and surface (Sandu et al., 2012). The processes of chemical alteration resulted from the interaction between the object and its environment are complication reaction, but also a series of allotropic modifications, with structural-crystalline reformations. In order to illustrate the degradation mechanism, one takes into account a series of many factors: the chemical composition of the basic alloy and the manufacturing technology of artifact, the physical-chemical and characteristics of the surrounding environment (Frame et al., 2013; Mircea et al., 2010; Robbiola and Hurtel, 1997).

This paper determines the composition, microstructure and manufacturing process of two inlaid metallic statuettes from 12th-16th century AD. Metalwork was a leading art form that effected decoration in other media for many centuries. Inlay with silver or gold seems to have become common from the twelfth century, but the popularity of the glittering brass statues probably also responded to a pious avoidance of gold and silver, which were avoided by the prophet. The Ayyubids (1171-1250) restored Egypt to Sunni orthodoxy (Allan, 2012; Garr, 2013). Then the death of the last Ayyubid ruler was followed by years of chaos in Egypt. From the turmoil a military leader emerged to start a new "dynasty". These new rulers reveal from the military slaves, mamluks, not as sons of sultans. Mamluk ruled Egypt for the next two hundred fifty years (1250-1517AD) (Islamic Art and Culture, 2004).

DOI: 10.12816 /mjaf.2019.25809

According to the analysis which performed on the statuettes; they were made of cast iron and inlaid with brass alloy. Cast iron used to describe an impure iron with 2-5% carbon in modern terms or with up to 1.9% carbon and other impurity elements such as phosphorus and silicon in antiquity. The earliest use of cast iron documented as early as the 4th century BC (Kostoglou and Navasaitis, 2006). Cast iron is not necessarily produced in a blast furnace. Iron casting was one of the products of African iron smelting and it was also re-produced in modern experimental smelting in bloomer shaft furnaces that use in ancient world (Greer, 2009). Copper knew to man much earlier than iron. In Egypt, copper was employed as far back as early pre-dynastic times. Brass alloy consisted of copper and zinc, copper recorded from pre-dynastic cemetery at Naqada containing 1.55% of zinc (Abd El-Rahman et al., 2013).

1.1. Description of two the statuettes

This paper presents the study of two statuettes. They were selected from the exhibition of faculty of fine arts museum in Cairo in Helwan University. The statuettes dated back to 12th-16th century AD; there were a lack of documentation in the museum's registration. (Fig. $1_{A,B,C,D}$) shows the first iron statuette with temporary number 28/7, it was formed by process of hammering; it took bird's shape and inlaid with copper. (Fig. $1_{E,F,G,H}$) shows the second iron statuette with temporary number 28/5, it took camel shape; it made by hollow cast and inlaid with copper. Both statuettes have flaking and detachment in the inlaid strips on the external surface and thick corrosion layers on the internal surface.

This study determines the effects of physiochemical alteration processes on inlaid iron statuettes by investigation the surface feature to identify the chemical composition of the bulk material and the manufacturing techniques of the statuettes. These investigations assist to understand the corrosion mechanism and the environmental effects on the deteriorations of the statuettes.

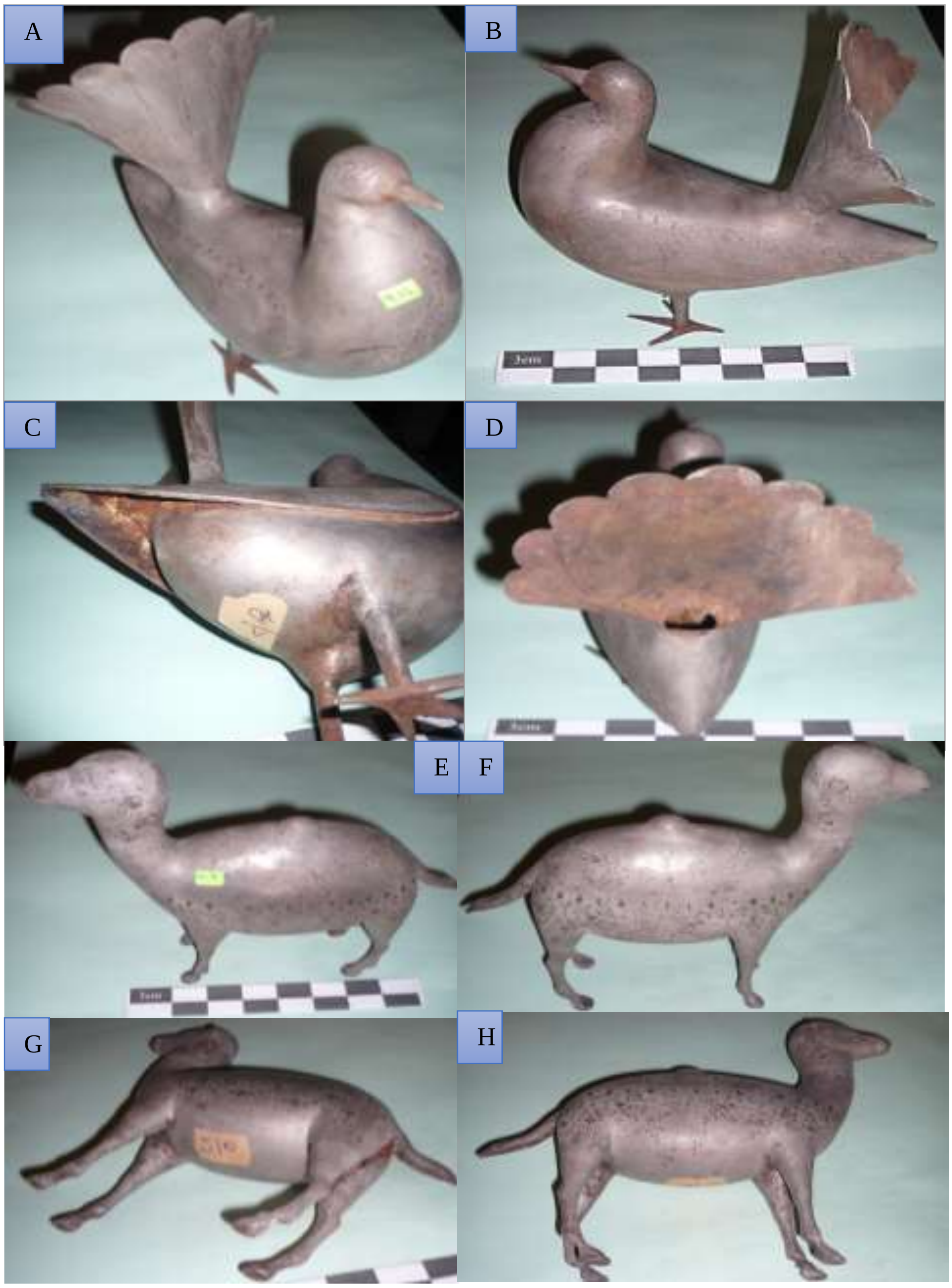

Fig. 1 (A,B,C,D) showed the first statuette; (A,B) showed the two sides of the bird statuette with many inscriptions, (C) showed the back of the statuette with layers of corrosion; (D) showed the solders in the statuette. Fig. (E,F,G,H) showed the second statuette; (E,F) showed the two sides of the camel statuette with many inscriptions, (G,H) shown other sides of the statuette with layers of corrosion.

2. EXPERIMENTAL METHODS

2.1. Optical Microscope (OM)

Microscopy investigation was performed with Smart-Eye USB Digital Microscope at various magnifications degrees, up to maximum 200X, for the investigation the morphological features of the surface and the corrosion products of the patina.

2.2 SEM-EDX Microscopy

Scanning electron microscopy (SEM) micro-graphs used to determine the morphology and composition of the alloy and the corrosion layers, model (EDAX AMETER materials analysis division. Quanta FEG250 X1 Analyzer), The Quanta QX1 EDAX detector was used for qualitative and quantitative micro-analysis. The EDAX detector is the third generation, the X-Flash; that does not require liquid nitrogen cooling and is about 10 times faster than conventional detectors Si (Li).

2.3 X-ray Diffraction (XRD)

The samples were analyzed to identify the corrosion products by X-ray Diffraction (XRD) method on a diffractometer PHILIPS PW 1710 for powder, under the following conditions: operating voltage: U = 40kV, current I = 30mA, X-rays from a copper cathode (Cu), wavelength Cu $K\alpha$ = 1.54178Å, graphite mono-chromator, test range: 4 - 90º 2θ, step: 0.02° 2θ, time constant: 0.5s (per step).

3. RESULTS AND DISCUSSION

The primary visual examination indicated that the first statuette (Fig.$1_{A:D}$) was made by using hammering processes; where, it observed solders in many positions in the body of the statuette as the end of the tail and in the top of its legs (Fig.1_{C}). There were inlays at all body drawing details like eyes and swings. The second statuette was made by hollow cast and inlaid with many inscriptions (Fig.$1_{E:H}$). Optical microscope image (Fig. 2) showed a heterogeneous crust of corrosion products and cracks in many parts of the internal surfaces on the two statuettes and flaking and detachment in the inlaid strips on the external surface.

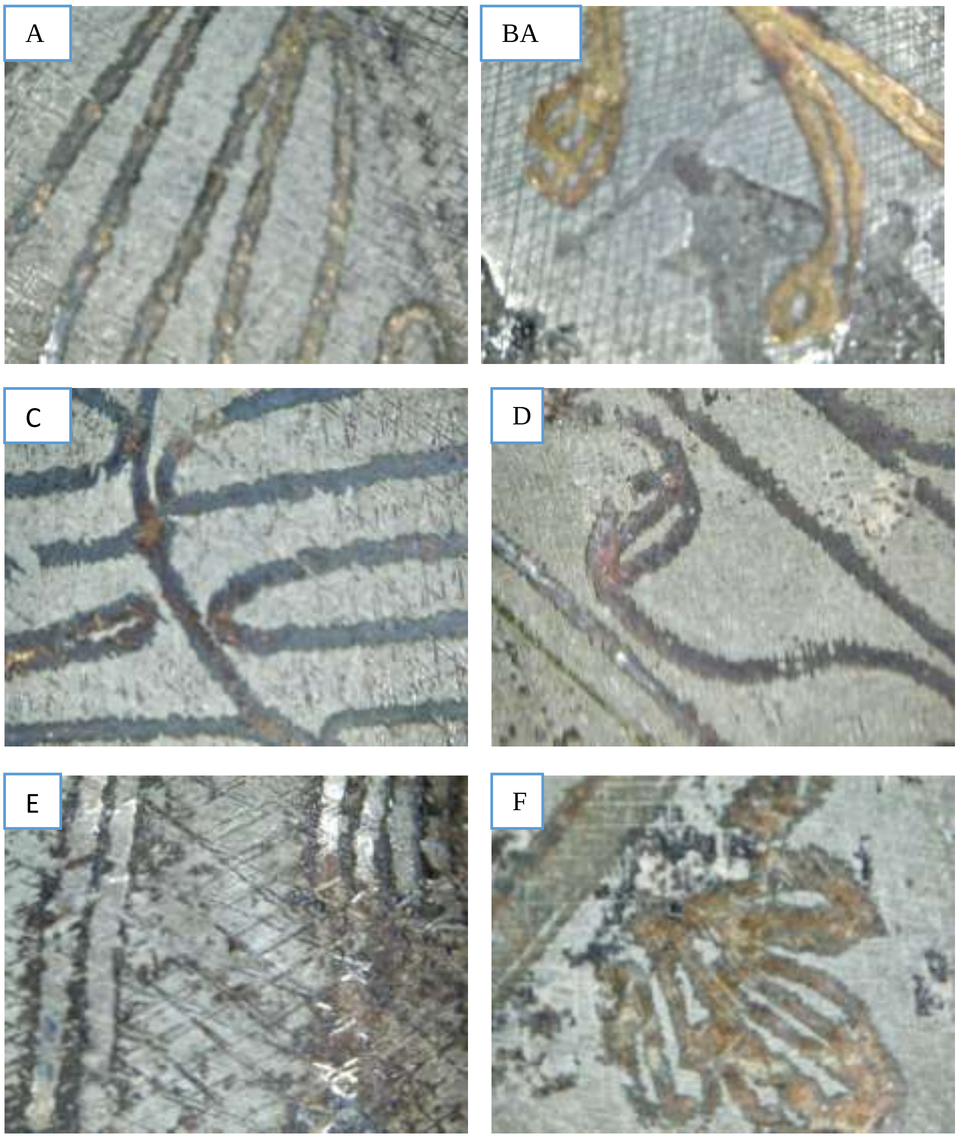

Fig. 2 Optical observation (200X) of the two statuettes (A,C,E) from the 1st statuette and (B,D,,F) from the 2nd statuette; (A,B) shown the copper strips in the two statuettes; (C,D) shown the flaking of the strips and appearance of the carbon layer of the organic adhesive; (E,F) shown the loss of copper strips and adhesive layer.

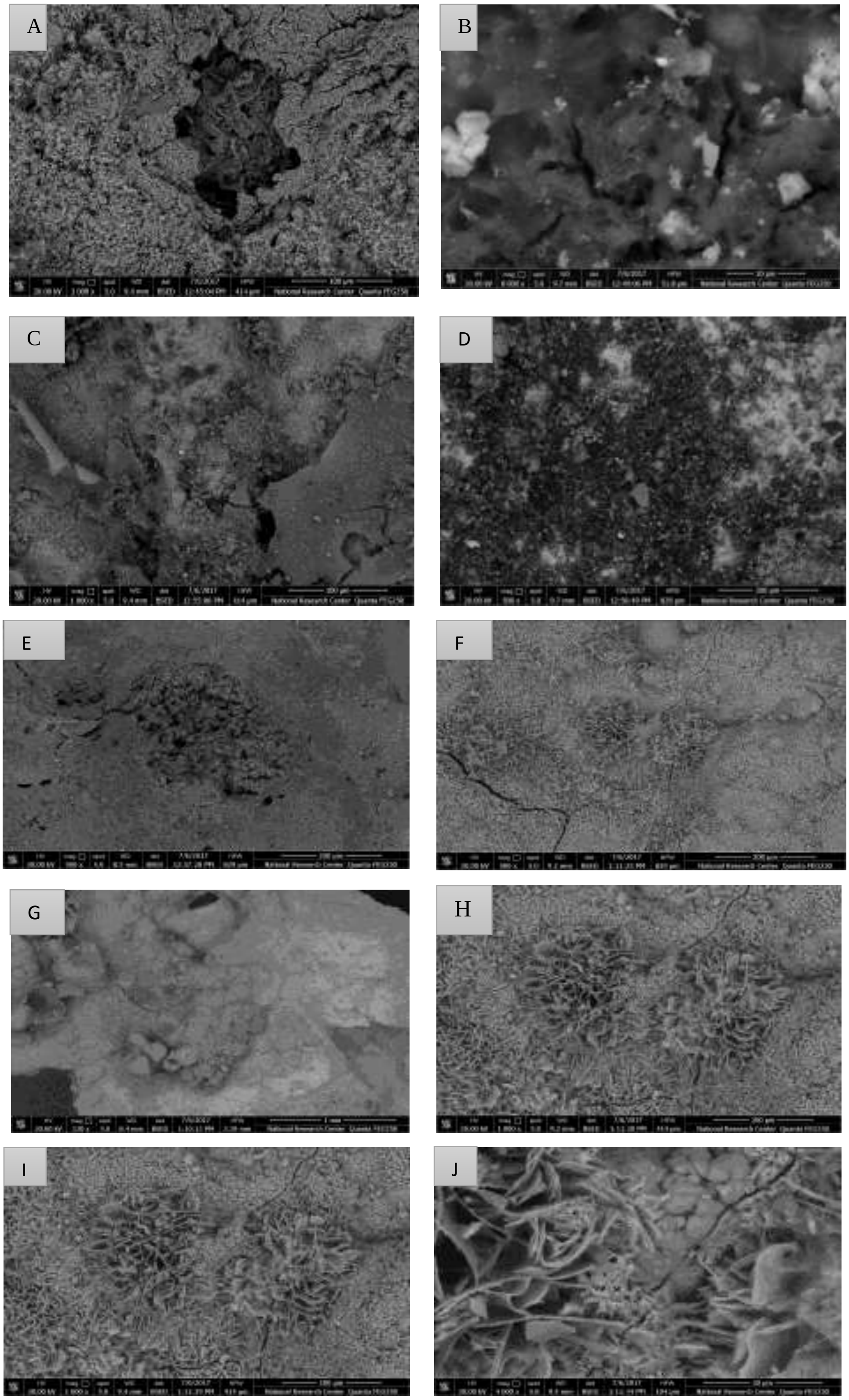

Fig. 3 shown the SEM images (A:D) from the 1st statuette and (E:J) from the 2nd statuette with different magnifications and structures.

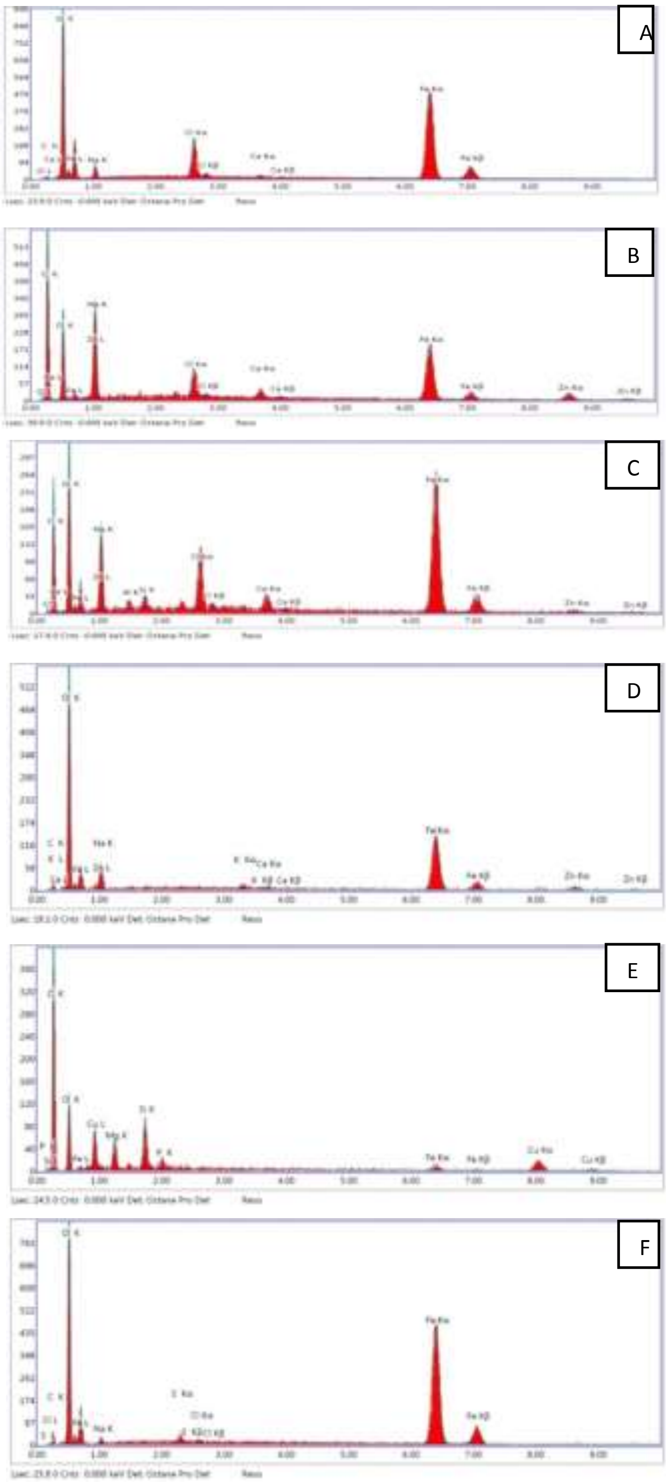

Fig. 4 EDX spectrums of samples shown composition of cast iron alloy inlaid with brass strips; (A,B,C) from the 1st statuette; (B) shown high content of carbon to indicate the organic adhesive used with brass strips; and (D,E,F) from the 2nd statuette, (E) shown copper to indicate with zinc in (D) to brass strips.

SEM microphotography (Fig. 3) showed a heterogeneous crust of corrosion products and cracks in many parts of the internal surfaces on the two statuettes. EDX analysis (Table 1and 2) and (Fig. 4) allowed identifying the nature of the alloy; where the body of the two statuettes consists of cast iron alloy (alloy of iron with approximately 1.9% carbon) and inlaid with brass alloy (alloy of copper with zinc). The raises of carbon in some samples indicated the use of organic adhesives in the inlays processes. Oxygen, sodium and chlorine ions present the corrosion products on the two statuettes.

Table1. EDX analysis of the patina which founded on the first statuette

Element	Weight %	Atomic %	Net Int.	Error %
C K	1.83	4.32	2.13	30.22
O K	31.49	55.77	187.87	8.15
NaK	5.96	7.35	19.86	15.64
ClK	5.68	4.54	77.06	7.06
CaK	0.49	0.34	5.43	39.98
FeK	54.54	27.67	277.03	2.93

Table2. EDX analysis of the patina which founded on the second statuette

Element	Weight %	Atomic %	Net Int.	Error %
C K	5.27	12.26	6.19	18.38
O K	30.69	53.6	157.37	7.89
NaK	2.52	3.06	6.25	22.48
S K	0.66	0.57	7.23	25.03
ClK	0.19	0.15	1.99	67.16
FeK	60.67	30.35	246.2	3.01

The x-ray powder diffraction patterns shown in (Table3 and Fig. 5) are representative of the patterns obtained from two samples of different corrosion products covering the two statuettes. The detected corrosion compounds of the first statuette revealed that the main constituents are Atacamite $Cu_2Cl(OH)_3$, Halite NaCl and Akaganite FeO(OH). In addition to Magnetite Fe_3O_4 and Iron sulfate $FeSO_4$ as minor ratio; and traces of Hematite (Fe_2O_3), Molysite $FeCl_3$, Iron silicate (Fe_2SiO_4) and Tenorite CuO.

The corrosion compounds of the second statuette consist mainly of Cuprite Cu_2O and Iron silicate Fe_2SiO_4. In addition to Goethite FeO(OH), Magnetite Fe_3O_4 and Halite NaCl as minor ratio.

Atacamite $Cu_2Cl(OH)_3$ and Halite NaCl were identified as the major compounds in sample 1 from the first statuette. Atacamite formed as a result of exposed Nantokite CuCl to moisture or moist air in saline environment; so Halite confirmed that the statuette existed in saline environment before transported to the museum.

Cupreous oxide CuO_2 (Cuprite) was detected as the major compounds in sample 2 from the second statuette. This confirmed that cuprite the first and most widely occurring alteration mineral of ancient copper and its alloy; formed as a result of exposure to oxygen or moist air. Cuprite is known to play a decisive role in the protectiveness of corrosion layers on copper.

But increase in oxygen pressure breaks its conformity and provoke its dissolution resulting in formation of flaws, through them carbon dioxide and other various gases and ions are able to penetrate that favor local cell activity leading to amassment of basic copper corrosion carbonates, chlorides, and sulphates . These corrosion products existed also in the inlays layers on the two statuettes (Kostoglou and Navasaitis, 2006). Iron silicate which founded in sample 2 because cast iron contains impurity elements such as silicon and phosphorus in antiquity.

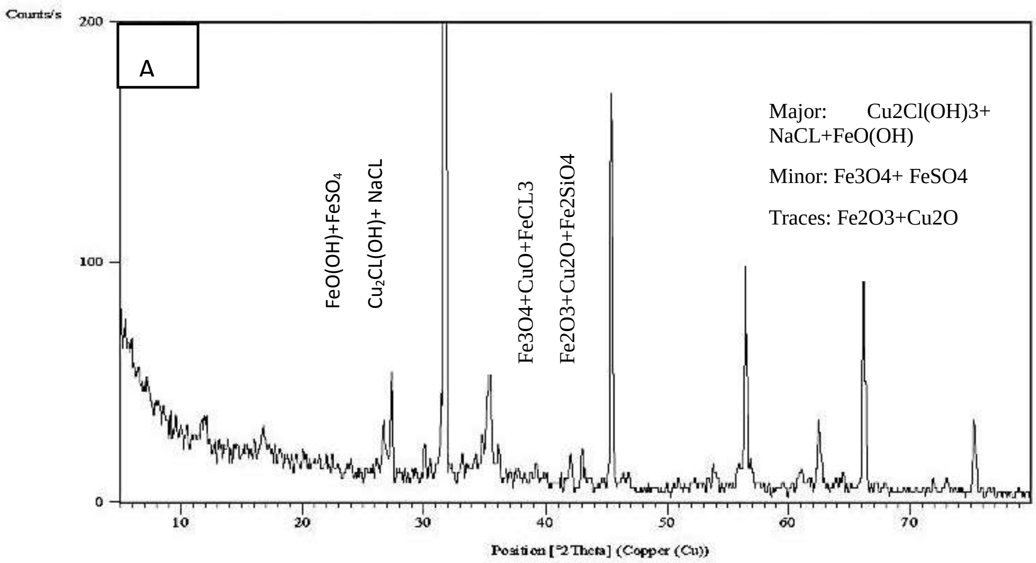

Fig. 5 shown the corrosion compounds of the two statuette by XRD; (A) from the 1st statuette which contains Atacamite $Cu_2Cl(OH)_3$, Halite NaCl and Akaganite FeO(OH) as a major minerals. In addition to Magnetite Fe_3O_4 and Iron sulfate $FeSO_4$ as minor ratio; and traces of Hematite (Fe_2O_3), Molysite $FeCl_3$, Iron silicate (Fe_2SiO_4) and Tenorite CuO. And Fig. (B) from the 2nd statuette which contains Cuprite Cu_2O and Iron silicate Fe_2SiO_4 as a major minerals; in addition to Goethite FeO(OH), Magnetite Fe_3O_4 and Halite NaCl as minor ratio.

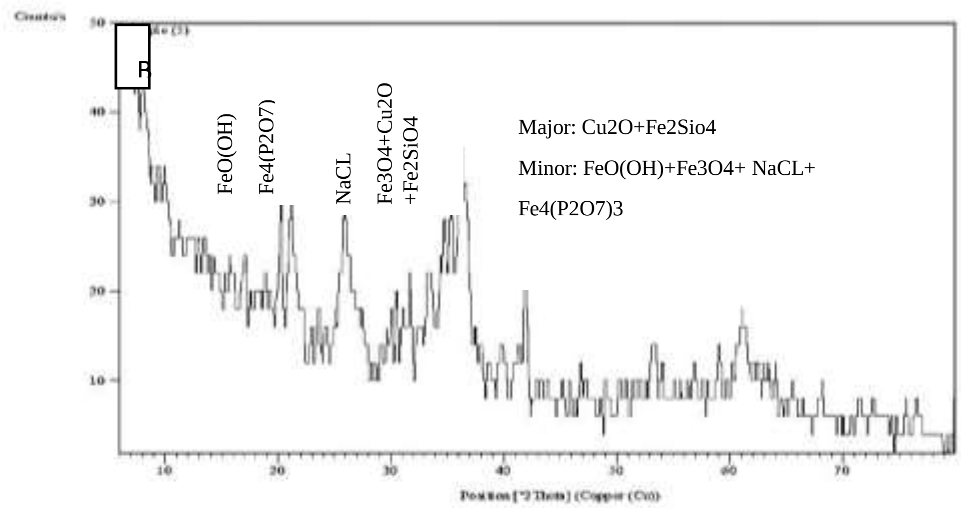

Table3. Mineral composition of corrosion products samples from the two statuettes by XRD

Minerals of the first statuette	Formula	Card No.	Content
Atacamite	$Cu_2(OH)_3CL$	02-0146	Major
Halite	NaCL	05-628	Major
Akaganite	FeO(OH)	34-1266	Major
Magnetite	Fe_3O_4	11-064	Minor
Iron sulfate	$FeSO_4$	01-0703	Minor
Hematite	Fe_2O_3	33-0664	Traces
Molysite	$FeCL_3$	01-1059	Traces
Tenorite	CuO	05-0661	Traces
Cuprite	Cu_2O	05-0667	Traces
Iron silicate	Fe_2SiO_4	12-0284	Traces
Minerals of the second statuette	Formula	Card No.	Content
Cuprite	Cu_2O	05-0667	Major
Iron Silicate	Fe_2SiO_4	12-0284	Major
Goethite	FeO(OH)	03-0245	Minor
Magnetite	Fe_3O_4	11-064	Minor
Halite	NaCL	05-628	Minor

Akaganite β-FeO(OH) iron oxy-hydroxide can be formed when the access to oxygen is increased; while the artifact get dry after excavation; the concentration of chloride ions in the corrosion products increase. Akaganite formation is an indication of active corrosion of iron under a layer of corrosion products. Chlorides, and sulphates ions causes the formation of molysite $FeCl_3$ and iron sulfate $FeSO_4$ (Reguer et al., 2009; Stahl et al., 2003).
Goethite α- FeO(OH) another iron oxy-hydroxide is a thermodynamically constant compound showing good protective properties, especially if it is in a form of fine particles. Magnetite Fe_3O_4 is the most common iron oxide identified on the archaeological iron, usually located next to the metal surface (Hoerle et al., 2004).
The corrosion products which formed in the hammering statuette are active and more than the corrosion products which formed in the hollow cast statuette. So we can say the manufacturing processes affecting on the deterioration processes in the two statuettes; where stresses are often introduced during manufacture which observed by microscopic examination in the form of propagation of some cracks. When ductile materials are deformed plastically at temperatures much below their melting point, they become stronger. This process is called cold-working (or strain-hardening), and it causes an increase in the dislocation density (Siano et al., 2006; Plekhanov, 2000; Shlimak, 1999). When a metal is worked at higher temperatures (hot-working), a little strengthening is achieved since the dislocations can rearrange themselves. However, strain-hardening is not always desirable, since ductility will be reduced. Restoring ductility by removing the effects of strain-hardening can be done by heat treatment, through recovery and recrystallization processes, and may be followed by grain growth (Jakielski and Notis, 2000; Sarabia-Herrero et al., 1996; Thornton et al., 2002).

CONCLUSION

The examination and analytical methods of two statuettes revealed that the first statuette is made by hammering while the second statuette is made using hollow casting techniques. The results revealed that the two statuettes are made of cast iron alloy and inlaid with brass alloy. This paper presented the evolution of physiochemical alteration processes on the two statuettes with respect the manufacturing processes which affecting on the deterioration processes, where the corrosion products in the hammering statuette are active and more than the corrosion products which formed in the hollow cast statuette.

Visual and microscopic examination showed massive compact layer of rust colored corrosion products in the internal surfaces of the two statuettes and flaking and detachment in the inlaid strips on the external surfaces. Analysis of the corrosion products indicated that the corrosive attack as a result of interaction between their components and the corrosive chloride ions coming from the surrounding environment. In first statuette sodium chloride allows the development of copper chloride and existence of iron chloride, the corrosion products also contained akaganite and a lesser extent of iron sulfate. In second statuette the dominated phases of goethite and magnetite explains the stability of base metal (iron) after excavation. The presence of corrosive ions may allow for more rapid cracks growth and flaking in inlaid strips. The study suggests preservation and protection the two statuettes rapidly to display the statuettes in the museum without causing further damages.

Acknowledgements

Thanks to the dean of Applied Arts Faculty, in Helwan University, Cairo, Egypt; for allowing studying Inlaid Iron Statuettes in the museum of the Faculty of Applied Arts in Cairo.

REFERENCES

1-Abd El-Rahman, Y., Surour, A.A., El Manawi, A.H.W., Rifai, M, Abd El Motelib, A., and El Dougdoug, A.M. “Ancient mining and smelting activities in the Wadi Abu Gerida area, central eastern desert, Egypt, preliminary results”. Archaeometry, 55, (2013) : 1067-87.

2- Allan, J.W., *Metalwork and material culture in the Islamic world art, craft and text*, London: L.B. Tauris., 2012, p.p132-133.

3- Frame, L.D., Freestone, I.C., Shu Yan Zhang, and Nicholas, M. “The effects of corrosion and conservation treatments on non-destructive neutron diffraction analysis of archaeological copper alloys: preliminary results”. Archaeometry, 55, (2013): 68-80.

4- Garr, A.H. *The Cleveland museum of art, Islamic art: By medium and motif,* The Cleveland museum of art, Boulevard Cleveland, 2013, p.p3:7.

5- Greer, S.E. *A comparison of the ancient metal casting materials and processes to modern metal casting materials and processes,* Rensselaer Polytechnic Institute, Hartford Connecticut, 2009.

6- Hoerle, S., Mazaudier, F., Dillmann, Ph., and Santarini, G. “Advances in understanding atmospheric corrosion of Iron; Mechanistic modeling of wet-dry cycles”. Corrosion Science, 46, (2004), 1431-65.

7- Islamic Art and Culture, A resource for teachers, National Gallery of Art, Washington, 2004, p.p.10-11

8- Jakielski, K.E., and Notis, M.R. “The metallurgy of Roman medical instruments. Materials Characterization”, 45, (2000): 379-89.

9- Kostoglou, M., Navasaitis, J. "Cast iron in ancient Greece: myth or fact?". Mediterranean Archaeology and Archaeometry, 6, 2, (2006):53-56.
10- Mircea, I., Sandu, I., Sarghie, I., and Sandu, A.V. "The identified effects of degradation in archaeological artifacts with overlapped metals used in authentication". International Journal of Conservation Science, 1, 1, (2010): 27-40.
11- Mircea, O., Sandu, I., Vasilache, V., and Sandu, A.V. "Applications of optical microscopy and energy-dispersive x-ray spectroscopy in the study of a pendant from the 2^{nd} – 3^{rd} century A C", International Journal of Conservation Science, 4, (2013): 701 – 709.
12- Plekhanov, V. *Isotope effects in solid state physics, Semiconductors and Semimetals*, vol.68, San Diego: Academic Press, , 2000.
13- Reguer, S., Mirambet, F., Dooryhee, E., Hodeau, J., Dillmann, p., and Lagarde, P. "Structural evidence for the desalination of akaganeite in the preservation of iron archaeological objects, using synchrotron x-ray powder diffraction and absorption spectroscopy", Corrosion Science, 51, (2009): 2795-2802.
14- Robbiola, L., and Hurtel, L.P. Standard nature of the passive layers of buried archaeological bronze, the example of two Roman half portrays: Metal 195 International conference on metal conservation, London, James and James Science Ltd, 1997, 109-117.
15- Sandu, I.G., Mircea, O., Vasilache, V., and Sandu, I. "Influence of archaeological environment factors in alteration processes of copper alloy artifacts". Journal of Microscopy Research and Technique, 75, (2012): 1646-52.
16- Sarabia-Herrero, E.J., Martin-Gil, J., and Martin-Gil, F.J. "Metallography of ancient bronzes: study of pre-Roman metal technology in the Iberian peninsula". Materials Characterization, 36, (1996): 335-47.
17- Shlimak, I.S. "Neutron transmutation doping in semiconductors: science and applications", Physics of the Solid State, 41, (1999): 716- 19.
18- Siano, S., Bartoli, L., Santisteban, J.R., Kockelmann, W., Daymond, M.R., Miccio, M., and De Marinis, G. "Non-destructive investigation of bronze artifacts from the Marches National Museum of Archaeology using neutron diffraction". Archaeometry, 48, (2006): 77-96.
19- Stahl, K., Nielsen, K., Jiang, J., Lebech, B., Hanson, J., Norby, P., and Lanschot, J. "On the akaganeite crystal structure, phase transformations and possible role in post-excavational corrosion of iron artifacts". Corrosion Science, 45, (2003): 2563-75.
20- Thornton, C.P., Lamberg- Karlovsky, C.C., Liezers, M., and Young, S.M.M. "On pins and needles: tracing the evolution of copper-base alloying at Tepe Yahya, Iran, via ICP-MS analysis of common-place items", Journal of Archaeological Science, 29, (2002): 1451-60.
21- Valério, P., Soares, A.M.M., and Araújo, M.F. "Middle bronze age arsenical copper alloy in southern Portugal", Archaeometry, 58, 6, (2016): 1003-23.