An Early Egyptian Copper Basin: Characterization and Case of Warty Corrosion

Yussri Salem*
Conservation Department, Faculty of Archaeology, South Valley University, Qena 83523, Egypt
Email: yousry.ali@arch.svu.edu.eg

Manal Ahmed Maher
Researcher in Post Graduate Studies College of Nanotechnology, Cairo University; Head of Computed Tomography X-Ray unit, Cairo Egyptian Museum, Ministry of Antiquities, Egypt
Email: manal.a.maher@gmail.com

* (Corresponding author)

Received: 21 December 2021
Revised: 17 January 2022
Accepted: 20 January 2022
Published: 25 January 2022

How to Cite

Abstract
The work aims to study the manufacturing technique, microstructure features, and morphology and mechanism corrosion of a hammered copper basin belonging to one of the early metallurgy ages in ancient Egypt (the old kingdom). The examination and analysis were carried out by USB microscope, polarized light microscope, scanning electron microscope equipped energy dispersive X-ray and X-ray diffraction. The results revealed that the basin was made of pure copper metal and manufactured as one piece by a hammering method. Metallographic examination showed a recrystallized microstructure, composed by the mechanical process for manufacturing the basin throughout hammering and annealing. The cylindrical body (rim) was in well-preserved state although it was covered with a thin layer of usual green corrosion products. The pustules of warty corrosion were formed on the inner surface of the rim. The curly shape of malachite corrosion were also observed. The morphology and mechanism of warty corrosion were presented and the difference between this type and the pitting corrosion was discussed. The characterization of the basin contributed to understanding and evaluating the preservation condition, which contributes to choosing the appropriate conservation process.

Keywords: Basin; Warty corrosion; Curly malachite; Copper; Hammering technique.

1. Introduction
With the end of the Neolithic Age, a great development occurred in human civilization since mining and extracting metals were known. Copper and gold are the first metals known in human civilization (Radetzki, 2009; Scheel, 1999). There is disagreement among scientists about determining which of the two metals had been first known (Radetzki, 2009; Thompson, 1958), while they agreed to name this period the Calchothic age, referring to the use of copper beside stone (Lucas and Harris, 1962). In ancient Egypt, the earliest practice of copper dates back to predynastic [5000 BC] where the earliest objects of copper have been found in the tombs of this age (Baumgartel, 1960). Metalworking in this period was limited and the objects were isolated occurrences of beads and bracelets, beads, pins and drills (Brunton and Caton-Thompson, 1928; Lucas and Harris, 1962). Therefore, it can be suggested that this period represents the Calchothic Age in Egypt. As the beginning of Naqada III cultures [3300 BC], Late predynastic age, and until the early Bronze Age, scientists tend to call this period with Copper Age since copper became more common (Arbuckle, 2021; Ashkenazi and Fantalkin, 2019; Baumgartel, 1960; William, 1964). The copper objects of Naqada III cultures were tools for agriculture, construction, hunting, and utensils for the daily use (Holmes, 1988; William, 1964) The predominant manufacturing method in Naqada III was by open-mold casting. At the beginning of the dynastic Period in Egypt (3050 BC), metal-processing techniques have been continuously

1
developed (Baumgartel, 1960; Lucas and Harris, 1962), the copper was common used and metalworkers mastered the manufacturing by cold-work/hammering beside casting method (Gänsicke et al., 2003). Moreover, the first sources of pictorial and inscriptive relating to the metal-working have appeared on the tombs of this period. Generally, the tools of the Calcolithic and copper age were made of pure copper and some of them showed the presences of arsenic that attributed to the use of copper ores including arsenic such as enargite Cu₃AsS₄ (Weinstein, 1974). Hammering was the manufacturing method of the copper tools of the chalcolithic age and subsequent ages preceding knowledge of other metals and alloys (Gänsicke et al., 2003; Weinstein, 1974). Pure copper is malleable and ductile, so it can be manufactured by hammering. The ancient Egyptians had high skill and mastered manufacturing the metallic objects by hammering (Odler et al., 2021). The hammering process was depicted for the first time in the 5th Dynasty in Niankhkhnum and Khnumhotep's tomb (Baumgartel, 1960). The relief depicted hammering of a copper sheet to form a basin.

This work presents a study of one of the hammered copper objects belonging to the Copper Age in ancient Egypt. The study of hammered copper objects from the Copper Age is very interesting. This importance was attributed to the age (old Kingdom), chemical composition (pure copper) and manufacturing technique (hammering). Moreover, the corrosion morphology of the studied basin provided additional importance to the study, where one of the less common corrosion morphologies was formed on the basin. The warty corrosion was spread over the basin that had a well-preserved original surface. The warty corrosion is local corrosion and expresses the formation of corrosion pustules on the metallic surface (Bonomi et al., 2003). It has been suggested that this type of corrosion appears only on copper alloys that contain high tin (Bonomi et al., 2003), the studied basin was made of pure copper. Little literature showed this corrosion type (Scott, 1994) but it is more likely to be noted in the restoration laboratories than in the presented literature. Some studies reported that there are two distinct forms of warty corrosion (Bonomi et al., 2003; Scott, 1994). The corrosion pustules in the first type are associated with cuprous chloride or the copper trihydroxychlorides and the mechanism of formation is attributed to localized corrosion processes enhanced by the presence of chloride ions in the environment. The second type is associated with cuprite and malachite and may tin-oxide-enriched patinas but no chloride ion content (Scott, 1994). In this regard, the work aims to a deeper understanding of the morphology and mechanism of warty corrosion. Finally, the results should be helpful in developing treatment strategies to copper artifacts.

2. Materials and Methods

2.1. The Description of the Studied Basin

The copper artifacts such as ewer, basin, and bowl are common archaeological finds from the old kingdom (2613-2181 B.C.) of the ancient Egypt (Ibrahim and Maher, 2018; Maddin et al., 1984). The studied basin dates back to the fifth dynasty of the old kingdom and is preserved in Egyptian Museum in Cairo under No. Cg 3476 (Fig. 1). The basin was excavated at Upper Egypt in the Edfu by the school of Mediterranean archaeology and French Institute of Oriental archaeology in 1937. The basin has a round base, with a horizontally executed rim and flange curved outward. This shape is common of the old kingdom's basins and may be inspired by a lotus flower. The rim height was 10.5 cm, the diameter at the base was 5 cm and gradually increased toward the flange up to 6 cm. Copper basins were widely used in the Old Kingdom in houses and temples for preserving liquids and washing hands (Ibrahim and Maher, 2018). Likely, early basins were relatively flat or less depth compared to the studied basin (Maddin et al., 1984).

![Figure-1. General view from all sides of the studied basin](image)

2.2. The Methods of Analysis and Investigation

Four cross-sections samples, one of them containing a corrosion pustule, were taken for the analysis and investigation. The examination was carried out by USB digital microscope and polarizing light microscope (PLM). The scanning electron microscope equipped energy dispersive X-ray (SEM-EDX) was also used for the elemental analysis of the cross-sections. Also, seven samples from superficial corrosion as well as a soil sample adhered to the
3. Results
3.1. Theoretical Background for Manufacturing Technique of Basins in the Ancient Egypt

In the old kingdom, the blacksmiths were highly skilled to raise complex three-dimensional basins manufactured as a single piece from a flat circular plate (Ojden, 2000). The pinnacle of skill is required for manufacturing such objects compared with a casting method or even the manufacturing by hammering of some objects such as menits, mirrors and weapons. Several sequential stages were carried to produce basins in ancient Egypt as follows:

3-1-1- The first step was the cast of a circular plate. The used sheets or plates in the manufacturing by the hammering were almost casted between two slabs of baked clay (terracotta) (Maddin et al., 1984; Maryon, 1949). For basins, the plate's diameter should be equal to twice the height of the rim plus the base's diameter. Also, a circular plate could be prepared by beating a metallic piece on a stone anvil (basalt, granite or diorite) as depicted on the walls of the Vizier Rekhmire's tomb (David, 2006; Gouda et al., 2007; Maddin et al., 1984).

2- The preparation of a hammering mold: Two molds for hammering basins were depicted on ancient Egyptian tombs. The first shape was depicted on Niankhkhnum and Khnumhotep's tomb, the old kingdom, as two wood pieces bound together. The second shape was depicted on the Rekhmire's tomb, the new kingdom, as a basin-shaped pattern (fig. 2a, b). By both types, a metalworker can reach the desired shape either by "sinking" it by blows on the inside of the basin or “raise” it by blows on the outside. The relief of Niankhkhnum and Khnumhotep's tomb is depicting the manufacturing process of a basin by hammering on wood anvil as shown in fig. 2a (David, 2006).

3- A hammering and annealing process: hammering and annealing would be repeated until the basin had attained the required shape. The first stage almost initialed hammering the basin's base in the center of a circular plate. While the circular plate rested on his anvil, the smith would direct his blows at the outer limits of the base circle in parallel with turning the circular plate, round and round the plate, until it become slightly convex on its underside and become a saucer-shaped bowl after a more hammering. Thereafter, by repeated beatings and annealing, a smith could "raise" the rim by blows on the outside. For an annealing process, metalworkers in ancient Egypt used the annealing process as early as the old kingdom period. Annealing improves ductile of metal during the hammering, while the cold beaten metal becomes hard so it is subjected to embrittlement and brittleness (Maryon, 1949; Weinstein, 1974). The relief of Niankhkhnum and Khnumhotep also depicted the annealing process (fig.1a). In this relief, a metalworker blows air into the fire and another one holds a basin above a charcoal fireplace. Also, the Hieroglyphic inscription in this scene descripts the annealing process (Hassaan, 2020).

4- Polishing and finishing processes; the ancient Egyptians used special stones to polish uneven patches on metallic surfaces. The surfaces may also have been finished using abrasives especially sand. Also, small balls made of felt or leather could be used to obtain a smooth surface (David, 2006; Lucas and Harris, 1962; Maddin et al., 1984). The polishing and finishing process in the old kingdom were depicted on a wall relief in the causeway leading to the king Unas' pyramid at Saqqara (the Fifth Dynasty) (Maddin et al., 1984). Also, a similar inscription of the king Unas' scene was depicted on the Rekhmire's tomb as shown in Fig. 2c (Davies, 1943). The studied basin doesn't have any inscriptions or decorations whether on the base or body. However, the basin's surface is extremely distinctive by a good polishing process of the cylindrical part.

Figure-2. A relief from Khnumhotep and Niankhkhnum's tomb is depicting an annealing and manufacturing process of a basin (a). Two reliefs on the walls of the Vizier Rekhmire's tomb are depicting the polishing process of the metallic objects (b, c). Note the hammering mold in a and b.
3.2. Chemical and Microstructure Composition

The elemental analysis by SEM-EDX indicated that the basin was made from pure copper without the presence of arsenic that is sometimes found in copper artifacts of the early ages (Ibrahim and Maher, 2018). Iron was detected as impurity in the analysis spots of the metallic structure. The addition of an iron-ore flux to the smelt could be suggested to explain the presence of iron (Maddin et al., 1984).

The examination by polarizing light microscope of three cross-sections reflected the characteristic features of the manufacture by cold-working (Irina and Valerii, 2018) as shown in Fig. 3. The first cross-section showed recrystallized irregular grains of the homogeneous α-Cu phase due to cold-working with annealing stages (Kmošek et al., 2018; Oudbashi and Davami, 2014) (fig. 3a, b). There is no evidence of unchanged eutectoid phases besides the alpha phase. The recrystallized microstructure also showed the high deformation and non-uniform distribution of grain, typical of the hot-worked product (fig. 3a, b) (Oudbashi and Davami, 2014). Moreover, an around inclusion in black color is observed in this sample.

In the second cross-section, the grains appears fine and have relatively equal size (fig. 3c, d). This microstructure indicates a final annealing process of the basin above the recrystallization temperature. Also, the microstructure showed clearly inner corrosion pits wither as intergranular or intragranular corrosion (Anusha, 2016; Kmošek et al. (2018). The intergranular corrosion (Scott, 1990) was also observed as dark lines at the grains boundaries in the lower right side in fig. 3d.

The third cross-section showed the orientation of grains elongation that indicates hammering orientation, the twins lines was also appeared in the microstructure as confirmation of the recrystallized (fig. 3e, f).

3.3. The Corrosion Morphology of the Surface and the Identification of Products

The basin’s surface was observed in low magnification by USB microscope. The whole basin is quite covered with the usual corrosion products of copper-based artifacts. The cylindrical body was in a well-preserved state while the base was completely corroded and subjected to the loss in several areas especially at outer borders where the basin was convex from this area (Fig. 1). Two types of corrosion layers were observed on the surface of the cylindrical body: smooth, compact patina in dark green color and a rough, powdery layer in green color. Mud lumps of burial soil were also found over both two layers (Fig. 4). Some micro-cracks have appeared on the surface in the region between the base and the body. On the inner surface, corrosion pustules from the type of warty were randomly formed on most of the surface. This corrosion type will be presented in detail in the subsequent title.
The examination of the basin under a USB microscope showed masses of a fibrous, green corrosion product agglomerated on the surface as shown in Fig. 5. This shape, which is characterized by fibers with green color, is called Curly malachite. The curly shape of malachite was identified since 1987 (Fabrizi et al., 1987). The malachite in this shape consists of individual fibers in green color (Nienhuis et al., 2016). Curly malachite is not common on copper-based artifacts and its literature is very little (Fabrizi et al., 1987), but it is more likely to be observed in conservation laboratories by restorers than in the present literature. The curly morphology of malachite has been reported mostly on artifacts retrieved from tombs (indirect burial) (Nienhuis et al., 2016). It was suggested that curly malachite is formed as a result of the reaction between cupric ions and a supersaturated aqueous solution of carbonate ions. Thereafter, malachite nucleates are formed on the surface as a bundle of single-crystal fibers (Nienhuis et al., 2016). The fibrous morphology has also been identified of other corrosion products such as eriochalcite (CuCl₂.2H₂O) and nantokite (CuCl) (Fabrizi et al., 1987; Nienhuis et al., 2016).

For the identification of superficial corrosion, three powdery samples (S1-S3) taken from various areas were analyzed. The results showed that copper chloride hydroxides such as atacamite and paratacamite were prevailing, malachite CuCO₃.Cu(OH)₂ and cuprite Cu₂O as well as quartz SiO₂ and gypsum CaSO₄.2H₂O were also identified as shown in Fig. 6a-c and table 1. Moreover, three samples (S4-S6) containing scraped pustules from several areas were analyzed, the results showed cuprite Cu₂O and atacamite CuCl.Cu(OH)₃ as corrosion products as well as two constituents from soil minerals: quartz SiO₂ and gypsum CaSO₄.2H₂O as shown in Fig. 6d-f and table 1. The remains of calcified burial soil on the basin's surface were also analyzed (S7) and results showed the presence of kaolinite Al₂Si₂O₅(OH)₄, quartz SiO₂, gypsum CaSO₄.2H₂O and microcline KAlSi₃O₈ (Fig. 6g).

<table>
<thead>
<tr>
<th>No.</th>
<th>description</th>
<th>location</th>
<th>identified products</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>Pale-green corrosion from the inner surface of the basin's base</td>
<td></td>
<td>atacamite (Ata) cuprite (Cup) gypsum (Gyp)</td>
</tr>
<tr>
<td>S2</td>
<td>Bluish-green corrosion mixed with pale-green corrosion located close to the basin's base</td>
<td></td>
<td>atacamite paratacamite (Par) malachite (Mal) quartz (Mal)</td>
</tr>
<tr>
<td>S3</td>
<td>Green corrosion product from the outer surface of the basin mixed with little of sand residues</td>
<td>atacamite malachite paratacamite cuprite gypsum</td>
<td></td>
</tr>
<tr>
<td>-----</td>
<td>-------------------------------------------------------------------------------------------------</td>
<td>-----------------------------------------------</td>
<td></td>
</tr>
<tr>
<td>S4</td>
<td>Corrosion pustules mixed with burial soil residues taken from the inner surface of the basin</td>
<td>atacamite cuprite gypsum quartz</td>
<td></td>
</tr>
<tr>
<td>S5</td>
<td>Corrosion pustules mixed with burial soil residues</td>
<td>cuprite atacamite gypsum</td>
<td></td>
</tr>
<tr>
<td>S6</td>
<td>Corrosion pustules mixed with soil residues. The sample from the outer surface of the basin’s base</td>
<td>atacamite cuprite gypsum</td>
<td></td>
</tr>
<tr>
<td>S7</td>
<td>Soil residues from the outer surface</td>
<td>kaolinite (Kao) quartz gypsum microcline (Mic)</td>
<td></td>
</tr>
</tbody>
</table>

**Figure-6.** XRD of superficial corrosion samples (a-c), pustules on the inner surface (d-f) and the remains of burial soil on the basin.
3.4. The Characterization of Warty Corrosion on the Basin

Both the well-preserved rim and severely corroded base were covered with a green corrosion layer and burial soil remains. Also, investigation of the basin's surface revealed the presence of a type of corrosion called “warty corrosion” over the entire basin (fig. 7a-c). This type is localized corrosion and describes the formation of corrosion pustules on surfaces of archaeological artifacts (Scott, 1994; 2002). The early classification of corrosion forms does not involve this corrosion type (Scott, 2002). In the last three decades, some literature involved warty corrosion while few studies suggested the mechanism and morphology of its occurrence (Bonomi et al., 2003; Brown et al., 1977; Megahed, 2014; Mortazavi, 2014; Newey, 1993; Novakovic et al., 2009; Scott, 1990; 1991; 1994). The first complete study of warty corrosion of bronze was presented by Bonomi et al. (2003). The pustules on the basin are rounded, compressed, and of different sizes. Some pustules were covered with a porous layer of green corrosion (fig. 7d, e). The pustules were randomly distributed over most of the inner surface of the basin. Removing some pustules and observing the zones beneath them showed that the green corrosion patina covering the surface is interrupted by a dark patina layer (fig. 7c.). Also, no pits or holes were observed beneath the pustules, so the boundary of the original surface was found although the metallic structure may be less dense than the original. Under USB, The base of each pustule, that presents the layer adjacent to the basin’s surface, was porous in a blackish gray color (fig. 7f, g). The base also showed zones in dark orange color as shown in fig. 7f. These orange zones among corrosion layers were reported as pure particles of redeposited copper (Wang and Merkel, 2001). The mechanism of redeposited copper is attributed to the electrochemical nature of corrosion as well as the limited solubility of aqueous species (Wang and Merkel, 2001). Accordingly, the presence of redeposited copper or unoxidized copper grains in the pustules especially at the base layer can be described as the electrochemical redeposition (i.e. reduction) of copper from cuprite corrosion.

A cross-section of a pustule under a USB microscope showed a layered structure (Fig. 7h) as follows: a dark layer under the original surface of the basin, a thick central layer over the original surface, and an external layer of fibrous green corrosion products. Metallic particles of the alpha phase were also observed at the outer extremity of the pustule under PM (Fig. 7h).

When the pustules had been scraped with a scalpel, layer by layer, cuprite corrosion in its reddish-brown color was always found within the pustules underneath the green layer (Fig. 8). Elemental analysis by EDX was carried out of the cross-section sample containing a pustule as shown in Fig. 9 and table 2. The results showed that the area under the original surface underneath the pustule mainly consists of Cu with few proportions of O. The oxygen indicates that internal oxidation has occurred in the area below the pustule. The pustule itself over the OS showed the presence of O and Cl, this indicates that the main constituents of the green corrosion phases are copper chlorides. The EDX detected also Si, Al, Mg and Ca, as shown in spot 3. These elements are attributed to soil minerals captured in the corrosion layer. The analysis did not detect any concentration of a carbon element, so these pustules are of the type of warty corrosion associated with chloride ions (Scott, 1994; 2002).

Figure-7. photos and macrographs of the pustules of warty corroson, (a, b) the pustules shape on the surface, (c) the bases of the pustules with the view of the original surface below them, (d, e) two pustules under USB microscope, (f) particles of redeposited copper at a pustule's base, (g) USB of a pustule's base, (h) PLM of a cross-section sample containing a pustule
The literature reported that pustules of warty corrosion are related to two formation mechanisms: first type is associated with a corrosion phase of cuprous chloride or copper trihydroxychlorides. These corrosion products often form as the central layer between the superficial layer and the pustule's base. The second type of warty corrosion is related to cuprite and malachite and this type may be associated with tin-rich phases. For the studied object, the EDX of pustules did not detect carbon element, so the second type could be suggested of the studied pustules. Likely, the pustules began with the formation of cuprite Cu$_2$O that locally occurred as a result of the superficial deposition of cuprous ions and sequential oxidation. After that, a reaction between cuprite and chlorine ions of burial soil was occurred and a superficial green corrosion layer was formed over pustules (Fan et al., 2020).

![Image](image_url)

**Figure-8.** the pustules reveals cuprite corrosion that forms the inner core

![Image](image_url)

**Figure-9.** SEM-EDX of one of corrosion pustules

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Al</th>
<th>Si</th>
<th>S</th>
<th>Cl</th>
<th>Ca</th>
<th>Fe</th>
<th>Cu</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>area scan</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.88</td>
<td>99.12</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Spot 1</td>
<td>7.07</td>
<td>0.00</td>
<td>1.79</td>
<td>0.00</td>
<td>1.51</td>
<td>0.00</td>
<td>0.62</td>
<td>89.01</td>
<td>100</td>
</tr>
<tr>
<td>Spot 2</td>
<td>27.75</td>
<td>0.00</td>
<td>0.00</td>
<td>1.00</td>
<td>6.53</td>
<td>0.00</td>
<td>1.78</td>
<td>62.93</td>
<td>100</td>
</tr>
<tr>
<td>Spot 3</td>
<td>14.26</td>
<td>16.16</td>
<td>11.01</td>
<td>9.85</td>
<td>4.90</td>
<td>8.27</td>
<td>2.51</td>
<td>33.03</td>
<td>100</td>
</tr>
<tr>
<td>Spot 4</td>
<td>20.25</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>7.49</td>
<td>0.78</td>
<td>1.35</td>
<td>70.13</td>
<td>100</td>
</tr>
</tbody>
</table>

### 3.5. The Difference Between Warty Corrosion and Pitting Corrosion With a Cap

Pitting corrosion is a localized form like the warty and appears as pits or cavities in metallic materials (Lucey, 1972; Zhang and Ma, 2019). Seven various forms have been distinguished of the pits of the pitting corrosion (Bhandari et al., 2015). These shapes were divided into two groups as shown in Fig. 10: sideway pits (four, left) and trough pits (three, right) (Bhandari et al., 2015). Often, these pits appear with open mouth (un-covered with corrosion products). In some cases, the pits are filled with porous corrosion products at up to the level of an object’s surface or are covered with cap-shaped corrosion products; the latter shape is similar of warty corrosion (Lucey, 1972; Lytle and Nadagouda, 2010). Generally, the presence of pits or cavities underneath caps can be considered as main criterion for distinguishing between pitting and warty corrosion. Moreover, Based on the literature of both two types and the characterization of the studied pustules, there are several notes and aspects that can be taken into account for distinguishing between both two types as shown in the table 3 and Fig. 11.
<table>
<thead>
<tr>
<th></th>
<th>Pitting corrosion</th>
<th>Warty corrosion</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The morphology of pitting corrosion is mainly characterized by pits underneath an original surface whether the pits were covered with caps or not (Bhandari et al., 2015).</td>
<td>Warty corrosion is mainly characterized by pustules over a surface and no pits under its (Scott, 1991).</td>
</tr>
<tr>
<td>2</td>
<td>The reaction of pitting corrosion initiates the formation of small cavities, or pits then they gradually grow inward and can grow deep enough to perforate a metallic wall entirely in hollow artifacts (Angelucci et al., 1978).</td>
<td>The reaction of warty corrosion initiates the formation of small pustules over a surface then it gradually grows outward.</td>
</tr>
<tr>
<td>3</td>
<td>The pits always penetrate deeply into the metallic material and are mainly filled with two corrosion products: Cu(I, II)-chlorides adjacent the metallic and cuprite layer over its (Lytle and Nadagouda, 2010; Suh et al., 2016).</td>
<td>The area underneath pustules is less density in the metallic structure, where a little amount from cuprous oxide was detected.</td>
</tr>
<tr>
<td>4</td>
<td>The caps of pitting corrosion are relatively porous, have holes and cavities in the top in many cases and sometimes contains pure metallic copper (Lytle and Nadagouda, 2010; Suh et al., 2016).</td>
<td>There are no holes or cavities in pustules while pure metallic copper has been reported.</td>
</tr>
<tr>
<td>5</td>
<td>When caps form on pits, they consist mainly of Cu(I, II)-chlorides and/or basic copper carbonates (Duthil et al., 1996; Lytle and Nadagouda, 2010).</td>
<td>The pustule consists mainly of cuprite corrosion as well as green corrosion products as a superficial layer whether thick or thin. In some cases, the whole pustule consist only of cuprite corrosion.</td>
</tr>
<tr>
<td>6</td>
<td>Corrosion products in pits can be cleaned as shown in Fig. 1. (Lytle and Nadagouda, 2010; Suh et al., 2016).</td>
<td>The area underneath the pustule is solid, coherent, and cannot be cleaned.</td>
</tr>
<tr>
<td>7</td>
<td>The formation of pitting corrosion based on the presence of chlorides-contain ions and the reaction with dissolved copper into cuprous (Cu⁺) and/or cupric (Cu²⁺) ions (Duthil et al., 1996; Suh et al., 2016).</td>
<td>The diffusion of cuprous ions (Cu⁺) on the surface and oxidation into cuprite corrosion is the first stage for forming pustules of warty corrosion (Scott, 1994; (Lytle and Nadagouda, 2010).</td>
</tr>
</tbody>
</table>

Figure-10. The seven forms distinguished of the pits of the pitting corrosion

Figure-11. Diagram of the common morphologies of warty corrosion (a) and pitting corrosion (b)

4. Conclusions
Several conclusions can be drawn from the study as follows:

- The studied basin has a high archaeological value that is attributed to the manufacturing technique, metallic composition, and the period to which the piece belongs. The basin was manufactured from the pure copper by hammering and dates back to the old-kingdom.
• Metallographic examination showed recrystallized irregular grains of the homogeneous α-Cu phase due to cold-working with annealing stages for manufacturing the basin.
• The basin showed various corrosion morphologies such as superficial and localized on the rim and complete mineralization of the base.
• Wart corrosion and curly malachite were formed on the inner surface of the basin and the formation mechanism of both of them was presented.
• The studied pustules of warty corrosion consisted mainly of cuprite corrosion that was covered by green corrosion products as a superficial layer.
• The study presented several aspects that could be used for the distinction between warty corrosion and pitting corrosion with caps because both are similar in shape.
• Understanding and diagnosing corrosion processes contributes to selecting the appropriate conservation and preservation methods for artifacts.

Acknowledgments
The authors thank Prof. Mohamed Abdel Rahman M. Moustafa, X-head of Non-Ferrous Metallurgy Department, Heat Treatment Department, Central Metallurgical R & D Institute (CMRDI) to help her in the metallographic examination of the cross-sections. They also thank Mr. Hamada Abdalla Abdalla the curator in Cairo Egyptian Museum for his agreement to study the studied object.

Declaration of Competing Interest
No potential conflict of interest was reported by the authors.

Funding
This research did not receive any external funding.

References


Lucas, A. and Harris, J. R. (1962). Ancient Egyptian materials and industries... Revised and Enlarged by JR Harris Edward Arnold.


