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## From Colour to Nanolayers: Corrosion in Egyptian Gold Work

Isabel Tissot, Lore Troalen, Maria Filomena Guerra\*

### Abstract

The aim of this project is to study a group of corroded Egyptian gold objects held in collections of the National Museums of Scotland, the Louvre Museum, and the Garstang Museum of Archaeology. The corroded surfaces with several areas of different colours were examined and the corrosion products identified using SEM-EDS and  $\mu$ XRF. It was suggested that the corroded surfaces are composed of Au-Ag-S-based compounds developed in a layer-by-layer structure. Elemental data associated to surface morphology suggested that the different surface colours are related not only to the thickness of the corroded layers, but also to the morphology of the corrosion products.

**Keywords:** gold, jewellery, corrosion, SEM-EDS,  $\mu$ XRF, layer-by-layer structure.

### INTRODUCTION

The red colouration observed on Egyptian gold objects has been reported as resulting from either the atmospheric corrosion or an intentional process. When corroded, gold objects show a dull appearance and a surface colour variation that ranges from dark yellow, rose, dark purple, and, sometimes, dark grey with an iridescent effect. In 1926, Alfred Lucas, the first author to describe the tarnishing of Egyptian gold objects, attributed the different surface colours to the presence of certain corrosion products formed due to the alloying elements (Lucas 1926, p. 266). According to Lucas, the dull and tarnished yellow surface is composed of silver and copper corrosion products, the grey gold surface contains silver chloride, and the reddish-brown colour surfaces contain iron and copper oxides.

Corrosion of Egyptian gold objects has been approached by other authors who identified on the corroded surfaces the presence of silver sulphide and gold-silver-sulphides (Frantz, Schorsch 1990; Rifai, el-Hadidi 2010). The different colour hues of the corroded surface were ascribed to the variation in thickness of the corrosion film. However, no full identification of the compounds that constitute the corroded layer was provided in these studies.

Recently, attempts have been made to identify and characterise the corrosion products that develop on the surface of gold objects exhibited in museums (Gusmano et al. 2004; Griesser et al. 2005; Changjiang, Chenghao, Peng 2007; Guerra, Tissot 2016; Tissot et al. 2019). The red coloured corroded surfaces have been mainly attributed to the presence of  $\text{Ag}_2\text{S}$ , but other corrosion products such as  $\text{CuS}$ ,  $\text{Cu}_2\text{S}$ ,  $\text{AuAgS}$ , and  $\text{Ag}_3\text{AuS}_2$  have also been identified. Notwithstanding, these studies do not consider the influence of the gold alloy composition on the corrosion mechanisms. Moreover, the relationship between the corroded surface and fabrication techniques of the objects, which can influence the corrosion rate and the corrosion layer morphology, was not searched.

The present work considers part of the research that was developed to shed more light on the understanding of corrosion of gold alloys. The results obtained for a group of corroded Egyptian gold objects are presented and the composition of the corrosion products and the relation between the surface alteration and the fabrication techniques are discussed.

## METHODS AND INSTRUMENTATION

### ANALYSED OBJECTS

Table 1 lists the eleven objects studied in this work. These pieces were selected based on their surface colour alteration and include three pieces of jewellery and eight fragments of gold foils. Two of the objects bear royal names: one is a cast signet ring bearing the name of Ahhotep; the other is a cartouche-shaped box bearing the name of Ahmose I, and is one of the three elements of an armband found by Auguste Mariette at Dra 'Abu el-Naga' on the breast of King Kamose (Guerra, Pagès-Camagna 2019). The third object is a biconical bead from Tomb 72, excavated at Haraga by Reginald Engelbach and Battiscombe Gunn for the British School of Archaeology in Egypt (Engelbach, Gunn 1923). This burial contained the body of a young girl and several jewellery pieces, including five gold catfish pendants and numerous gold beads today reassembled in five strings (Troalen et al. 2016). Finally, the fragments of gold foils included in this study come from gilded objects found in tombs thought to have contained the burials of Middle Kingdom individuals excavated between 1906 and 1909 by John Garstang in the so-called "North Cemetery" at Abydos (Snape 1987; Tissot et al. 2015).

Object	Provenance	Dynasty	Museum
armband & cartouche	Tomb of Kamose	18th	Louvre Museum
signet ring	cartouche of Ahhotep	17th/18th	Louvre Museum
Bead in a string	Haraga, tomb 72	12th	National Museums Scotland
Fragments of foil (8)	Abydos North Cemetery	12th	Garstang Museum of Archaeology

### ANALYTICAL METHODS

The bead and the foil fragments were analysed at the LIBPhys, Nova University of Lisbon, by X-ray fluorescence ( $\mu$ XRF) spectroscopy with a Bruker Tornado M4 equipped with a Rh tube (50 kV, 300  $\mu$ A) and a SDD detector (Tissot et al. 2015). The cartouche-shaped box and the signet ring were analysed by particle-induced X-ray emission (PIXE) using a 3 MeV proton beam at the AGLAE accelerator of the C2RMF in Paris (Lemasson et al. 2015; Guerra, Pagès-Camagna 2019).

The morphology and composition of the corrosion products that developed at the surface of the objects were analysed by scanning electron microscopy (SEM) combined with energy dispersive X-ray spectroscopy (EDS). The bead and the foils were analysed at the National Laboratory for Energy and Geology (LNEG), Lisbon, using a Philips XL 30 FEG model, and the cartouche and signet ring at the C2RMF in Paris using a FEI Philips XL 30 CP with controlled pressure. Image capture and X-ray spectra (collected in spot mode for a 300 s acquisition time) were obtained with acceleration voltages from 10 to 20 kV.

## RESULTS

### CORRODED SURFACE CHARACTERISATION

All the objects show a surface colour alteration; however, as illustrated in Figure 1, their gold base alloys are distinct, with Ag contents ranging between 2.2 wt.% to 40 wt.%, and Cu contents from 0 wt.% to 5.5 wt.%. Two distinct surface colour alterations were observed: 1) a homogeneous red coloration (Fig. 2a), and 2) a heterogeneous coloration with a colour variation between dark yellow, violet, blue until red (Fig. 2b). The signet ring, the cartouche, and the bead are in the first case, but the gold foils from Abydos show the two alterations.

The observation under the SEM of the foils with homogeneous coloration shows aggregates of small round particles forming a nanoporous layer (Fig. 3). Areas with more accentuated corrosion present hollow polycrystalline tubular formations randomly oriented on the top of the porous layer. EDS analysis of the corroded layer shows an increase of the Ag and S contents, suggesting the formation of Au-Ag-S-based compounds (Table 2). The areas with higher concentration of tubular formation have Ag contents higher than 20 wt.% and S content of 9 wt.%.

Figure 4a shows the heterogeneous colour alteration under the SEM. A regular nanoporous layer containing round particles constitutes the red area, which is morphologically similar to those observed on surfaces showing a homogeneous coloration. Three different layers (Fig. 4b) constitute the blue areas; the first is morphologically similar to the red corrosion areas, the second contains agglomerates of corrosion products, and the third thin tubes randomly distributed. This last layer corresponds to the areas with accentuated corrosion. EDS analysis shows an increase of the Ag and S contents that vary according to the distinct corrosion layers (Table 3). Silver reaches 54 wt.% in the blue corroded area and 80 wt.% in the red area.

### INTERGRANULAR CORROSION AND STRESS CORROSION CRACKING

Intergranular and stress corrosion cracking were revealed under the SEM for the bead from Haraga and for the cartouche bearing the name of Ahmose I. They are related to casting defects and to the use of production techniques that involved important thermo-mechanical deformations. The bead has a porous surface texture indicating that the annealing during the production process of the gold foil by hammering was incomplete (Fig. 5a). On the cartouche the corrosion develops along the grain boundaries or close adjacent regions while the bulk of the grains remain almost unaffected (as underlined by Forty 191) (Fig. 5b). This intergranular corrosion is often associated with chemical segregation effects or with the precipitation of specific phases along the grain boundaries (Downben, Miller 1987).

On the surface of both objects, the presence of other corrosion products, randomly distributed (Fig. 5b), suggests the development of an independent corrosion process. This may indicate an atmospheric corrosion process that begun during either burial or exhibition.

## DISCUSSION

The analytical results obtained in this work revealed the presence of several corrosion products that developed in a layer-by-layer structure on the surfaces of corroded Egyptian gold objects. Corroded surfaces with distinct morphologies, and thus containing distinct corrosion products, were reported for other gold objects (Guerra, Tissot 2016; Tissot et al. 2019).

However, the present study suggests that the colour of the corroded areas depend not only on the film thickness, but also on the distinct formed corrosion products.

Elemental data associated to each morphology revealed the formation of Au-Ag-S-based compounds instead of the expected Ag<sub>2</sub>S referenced as the main corrosion product for gold alloys (Bastidas et al. 2008). The elemental composition obtained from the corroded surfaces also suggests the formation of different corrosion products for distinct gold base alloys. However, in this study, it was not possible to disclose the influence of the base alloy composition on the nature of the formed corrosion products.

It was also shown that the fabrication techniques influence the intergranular corrosion and the development of stress corrosion cracking. These forms of corrosion can produce areas of reduced corrosion resistance and induce the localised formation of corrosion products. This contributes to the heterogeneous colouration of the surface.

The detailed description of the corroded surfaces, demonstrate that corrosion influences their colour and opens new research guidelines related to the study of Egyptian gold work. For example, this work has proven the need to identify whether the coloured gold alloys surface is a result of an intentional process or of an atmospheric corrosion phenomenon. This distinction is essential in order to identify the techniques used to create red-coloured surfaces and to assess the conservation state of the objects.

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## CAPTIONS

Fig. 1. Ternary diagram representing the Au, Ag, and Cu contents in wt.% for the group of objects analysed by EDS and  $\mu$ XRF (Tissot et al. 2015; Lemasson et al. 2015; Troalen et al. 2016).

Fig. 2. a. Biconical gold beads from one of the five strings found in an intact burial of a young girl in Tomb 72, Cemetery A at Haraga, dating to the mid-late 12th Dynasty; and detail of one bead showing a homogeneous red colour surface. b. Gold foil fragments from a tomb at Abydos cemetery. These were probably attached to a wooden artefact destroyed by burning; and detail of one foil showing a heterogeneous colouration surface. © M.F. Guerra/CNRS

Fig. 3. a. SEM-SE image of the homogeneous red corroded surface of a foil from Abydos. b. SEM-SE image of a detail of the polycrystalline tubular formations.

Fig. 4. a. SEM-SE image of the surface morphology of the red corroded area of a foil from Abydos. b. SEM-SE image of the surface morphology of the blue corroded area of a foil from Abydos. 1–3 corresponds to the 1st, 2nd, and 3rd corrosion layers.

Fig. 5. a. SEM-SE image of the surface of the bead fragment from Haraga showing its porosity and preferential corrosion. b. SEM-SE image of the cartouche bearing the name of Ahmose I showing the intergranular corrosion.

Table 1. List of the studied objects with the information of their provenance, chronology, and local of conservation.

Table 2. Elemental composition by EDS (wt.%) normalised to 100% of the base alloy and corrosion layer of a foil from Abydos showing a homogeneous coloration.

Table 3. Elemental composition by EDS (wt.%) normalised to 100% of the base alloy and corrosion layer of a foil from Abydos showing a heterogeneous coloration.

## BIBLIOGRAPHY

Bastidas, D.M., Cano, E., González, A.G., Fajardo, S., Lleras-Pérez, R., Campo-Montero, E., Belzunce-Varela, F.J., Bastidas, J.M., "An XPS Study of Tarnishing of a Gold Mask from a Pre-Columbian Culture", *Corrosion Science* 50, 2008, pp. 1785–1788.

Changjiang, Y., Chenghao, L., Peng, W., "Investigation of the Tarnish on the Surface of a Panda Gold Coin", *Rare Metals* 26, 2007, pp. 68–73.

Downben, P., Miller, A., "Surface Segregation from Gold Alloys", *Gold Bulletin* 20, 1987, pp. 54–65.

Engelbach, R., Gunn, B., Harageh, BSAE 28, London, 1923.

Forty, A., "Micromorphological Studies of the Corrosion of Gold Alloys", *Gold Bulletin* 14, 1981, pp. 25–35.

Frantz, J.H., Schorsch, D., "Egyptian Red Gold", *Archeomaterials* 4, 1990, pp. 133–152.

Griesser, M., Traum, R., Mayerhofer, K.E., Piplits, K., Denk, R., Winter, H., "Brown Spot Corrosion on Historic Gold Coins and Medals", *Surface Engineering* 21, 2005, pp. 385–392.

Guerra, M.F., Pagès-Camagna, S., "On the Way to the New Kingdom: Analytical Study of Queen Ahhotep's Gold Jewellery (17th Dynasty of Egypt)", *Journal of Cultural Heritage* 36, 2019, pp. 143–152.

Guerra, M.F., Tissot, I., "Bronze Age and Iron Age Gold Torcs and Earrings from the Iberian Atlantic Façade: Non-Invasive Multi-Analytical Approach to the Characterisation of the Alloys and the Corrosion", *X-Ray Spectrometry* 45/1, 2016, pp. 5–13.

Gusmano, G., Montanari, R., Kaciulis, S., Montesperelli, G., Denk, R., "'Gold Corrosion': Red Stains on a Gold Austrian Ducat", *Applied Physics A* 79, 2004, pp. 205–211.

Lemasson, Q., Moignard, B., Pacheco, C., Pichon, L., Guerra, M.F., "Fast Mapping of Gold Jewellery from Ancient Egypt with PIXE: Searching for Hard-Solders and PGE Inclusions", *Talanta* 143, 2015, pp. 279–286.

Lucas, A., *Ancient Egyptian Materials and Industries*, London, 1926.

Rifai, M.M., el-Hadidi, N.M.N., "Investigation and Analysis of Three Gilded Wood Samples from the Tomb of Tutankhamun", in J. Dawson, C. Rozeik, M.M. Wright (eds.), *Decorated Surfaces on Ancient Egyptian Objects: Technology, Deterioration and Conservation*, Conference Acts, Cambridge, 7–8 Sept. 2007, London, 2010, pp. 16–24.

Snape, S., "Mortuary Assemblages from Abydos", vol. I, unpublished PhD Thesis, University of Liverpool, 1987.

Tissot, I., Troalen, L.G., Manso, M., Ponting, M., Radtke, M., Reinholz, U., Barreiros, M.A., Shaw, I., Carvalho, M.L., Guerra, M.F., "A Multi-Analytical Approach to Gold in Ancient Egypt: Studies on Provenance and Corrosion", *Spectrochimica Acta Part B* 108, 2015, pp. 75–82.

Tissot, I., Correia, J., Monteiro, O.C., Barreiros, M.A., Guerra, M.F., "When Gold Stops Glittering: Corrosion Mechanisms of René Lalique's Art Nouveau Jewellery", *Journal of Analytical Atomic Spectrometry* 34, 2019, pp. 1216–1222.

Troalen, L.G., Tissot, I., Maitland, M., Guerra, M.F., "Jewellery of a Young Egyptian Girl: Middle Kingdom Gold Work from Haraga Tomb 72", *Historical Metallurgy* 49/2, 2016, pp. 75–86.