The delamination of silversulphide layers

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Abstract

The morphology of a delaminating tarnish film formed on a 17th century showplate is examined by SEM-EDS. Three different layers could be observed; *i)* the silver copper alloy, *ii)* a copper sulphide layer and on top of that a *iii)* silver sulphide layer. The original alloy shows elongated copper particles within the silver matrix, indicating a milled metal. The copper sulphide layer consists of conglomerated particles, with islands of metallic silver and possibly some metallic copper. The silver sulphide layer is stratified and contains cracks. Inside this layer several cavities and island of metallic silver are observed. The overall thickness of the stratified Ag_2S layer is typically 14 µm, while the layers that make the stratification varies from 200 – 1250 nm. The maximum silver sulphide thickness will most likely be determined by the thickness of the original fine silver layer on the object and the alloy composition.

Keywords: Silver, silversulphide, delamination

1. Introduction

Tarnishing of silver is a problem encountered in many museums throughout the world. Different preventive and active conservation strategies have been developed to minimise tarnish films growth on historic silver objects, varying from lacquering to packing in polymer films. However, some people believe that tarnish films provide protection against further damage. This, in itself, is partly true. If the increase of weight of silver (or the silver sulphide layer thickness) for the reaction between silver and low concentrations of hydrogen sulphide, is plotted against the reaction time, a square root relation is obtained (Abbott 1974). This means that the reaction rate decreases when the silver sulphide thickness increases. This can be explained by diffusion of H_2S through the tarnish film, which becomes more difficult when the layer thickness grows. If silver is reacted with a mixture of H_2S and NO_2 a linear relation is obtained (Ishino, Kishimoto et al. 1980). In both cases a more or less infinite growth of tarnish films is expected, but never observed.

The morphology of silver sulphide films has not been studied extensively. Attention is focussed on silver sulphide layers formed at high pollutant concentrations, typically at ppm levels resulting in different types of crystals (Drott 1959; Drott 1960; Fischmeister and Drott 1959; Keil and Meyer 1960).

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Although the composition of tarnish films formed in the museum environment has been studied, the morphology of those films formed at ambient H_2S concentrations (ppt levels) has not been studied in detail.

The Rijksmuseum owns a '*Schauplatten*' (showplate) which shows the school of Athens[1] surrounded by busts of Poluxena, Zenopha, Sapho and Lucretia, and Music, expressed by eight muses playing various musical instruments. In some parts a clear delaminating tarnish layer is visible. The examination of the silver sulphide delaminating was aimed at the following issues:

- What is the composition and morphology of the tarnish layer?
- What is the typical thickness at which silver sulphide delaminates?

2. Experimental

The surface of the showplate has been examined by Leica optical microscopy using low magnification (typically 15x). Samples could easily be collected by removal of the already detached layers or by applying sticky tape directly on the tarnish surface. Cross sections were prepared according to techniques recommended by Struers™ [2]. The sections were embedded in epoxy resin, ground using waterproof paper (finish with 4000 grit), and polished with 6 and subsequently with 1 μm diamond spray.

The cross sections were examined using a JEOL- JSM 5910-LV scanning electron microscope (SEM) with a Vantage Thermo Noran energy dispersive spectroscopy (EDS) system at high vacuum and typically 20 kV accelerating voltage. Elemental mapping and analyses were conducted using EDS.

3. Results and Discussion

The plate has been in the possession of the Rijksmuseum Amsterdam since 1878. After many years in storage, the surface of the showplate is now covered by a thick black tarnish layer. This is assumed to be mainly silver sulphide (Figure 1A). As can be seen, this layer delaminates at certain places from the metal surface. At places where the silver sulphide is not present the metallic silver surface is observed (Figure 1B). On the revealed silver, new tarnish has been formed at places that were easily reached by H_2S when the tarnish was still present on the surface, *i.e.* the cracks in the Ag_2S. The black lines on the metallic silver in Figure 1B show the outline of the cracks in the original silver sulphide layer.

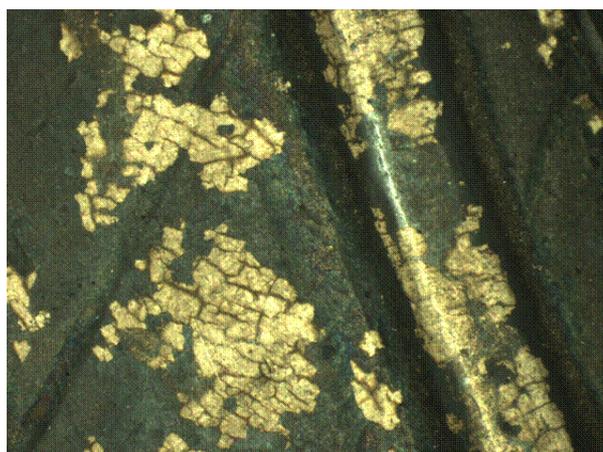Figure 1A: Detail of the surface of the showplate showing the thick tarnish layer with delaminating flakes.

Figure 1B: Detail of 1A, showing the outline of the cracks in the original sulphide layer.

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[1] The depiction is described as the School of Athens

[2] Instructions followed given through Struers (www.struers.com), abrasive grinding to 4000 grit, afterwards diamond polishing with 6 and 1 µm

Taking samples looked easy enough at first instance. Silver sulphide flakes could be removed by sticky tape. However, embedded cross sections of these, showed great disruption of the tarnish layer. One result of this way of sampling was that the boundary at which the silver sulphide flakes from the base could be analysed, showing only the presence of silver and sulphur without any copper. Samples were also taken by cutting a small section out of the rim of the object, leaving the tarnish layer still adhered to the metal surface. Polished cross sections of these samples were studied by SEM with EDS. The silver sulphide layer which seemed attached to the silver during mounting was in fact already detached. At low magnification it can be seen that at full length of the cross section the tarnish layer is not fully adhered to the metal surface. At higher magnification three different layers can be observed in the cross section (see Figure 2), *i)* the original alloy at the bottom, *ii)* with a dark layer on top and finally *iii)* a light grey stratified layer.

Figure 2: Back scattered image, silver, copper and sulphur mappings of the cross section.
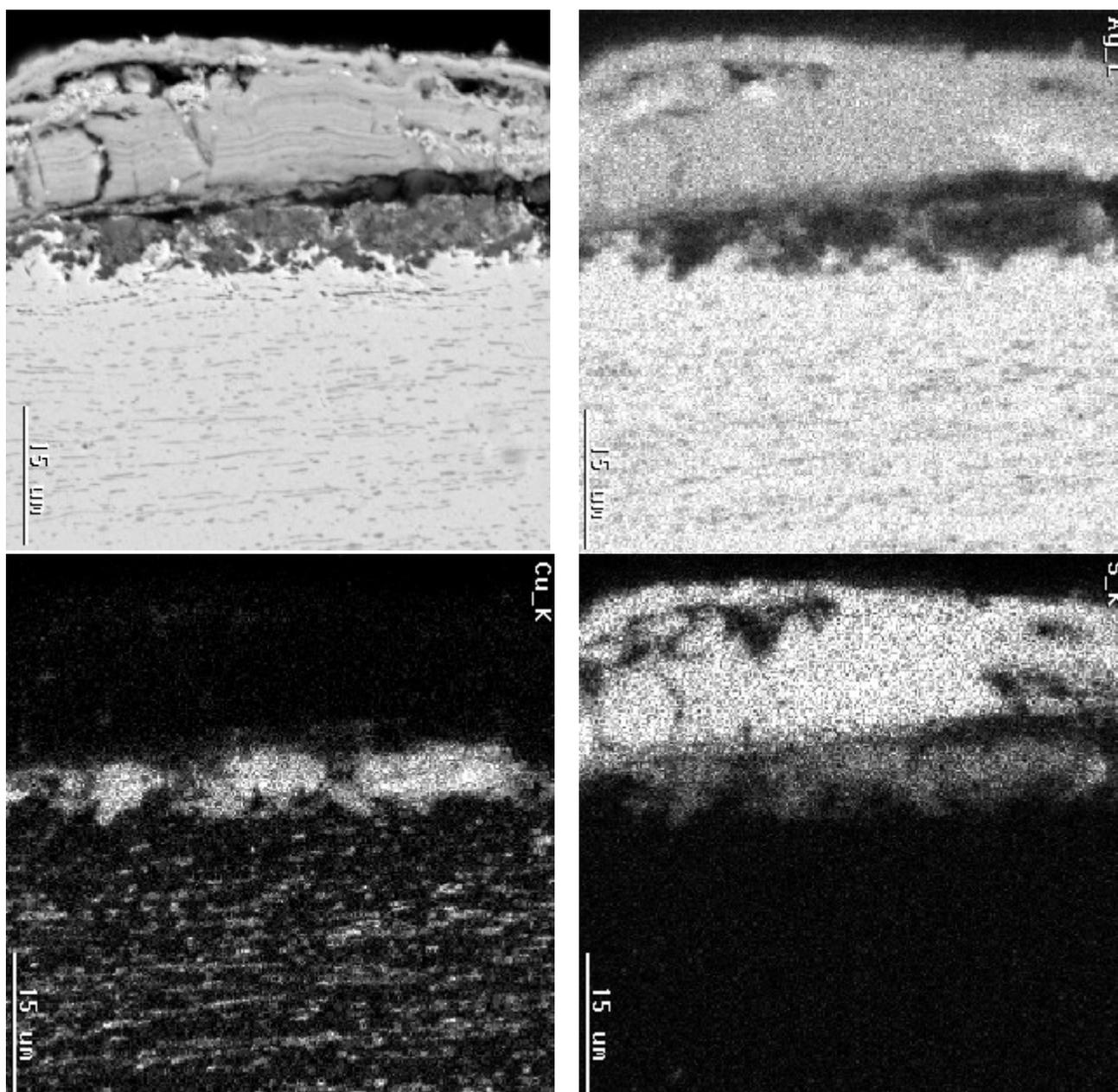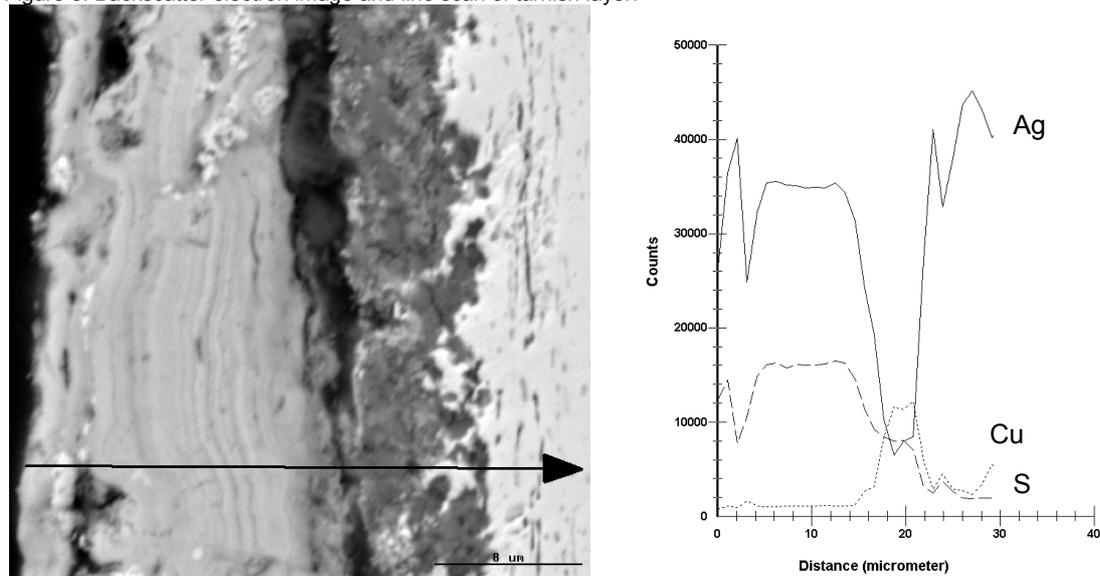
Figure 3: Backscatter electron image and line scan of tarnish layer.

The original alloy shows elongated copper particles within the silver matrix, indicating a milled metal. When this showplate came into the possession of the Rijksmuseum in 1878, it was accompanied by 571 other objects given through the bequest of F.G.S. Baron van Brakell tot den Brakell. This showplate was mentioned as being 'new' and therefore was considered to be manufactured in the 19th century. In the beginning of this research it was even thought that it could be an electrotype of the original of a 17th century showplate[3] which is owned by the Royal Museum for Art and History (Brussels). Thus far metal milling was supposed to have only taken place from the late 17th century onwards, yet already in 1551, King Henry II had bought a rolling mill for the mechanisation of coin striking in Augsburg (Jacobi 1982). Therefore this technique must have been already available during the 16th century in Germany. It should be noted that the size of the plate being 85 by 75 cm still requires further research, because it is surprising that objects of these dimensions could be manufactured with a rolling mill.

The second layer is rather heterogeneous; showing the presence of conglomerated particles (dark grey in the back scatter image of Figure 3), islands of metallic silver (white phase in the back scatter image of Figure 3), possibly metallic copper (black particles in the back scatter image of Figure 3) and the absence of cracks. The line scan indicates the presence of copper and sulphide, which is supported by the mapping presented in Figure 2. The presence of silver and / or silver sulphide made it impossible to determine the copper / sulphur ratio accurately; it is assumed that CuS is most likely formed (Scott 2002). The metallic silver islands are concentrated near the alloy. Nearer the top all silver has leached out and has been transformed into Ag_2S. The copper enrichment of this layer is remarkable. One might have expected the presence of remnant elongated copper particles (or copper sulphide particles) within the silver sulphide layer (see below for detailed description), which is not the case. The compositional separation of these two corrosion layers, *i.e.* silver sulphide and copper sulphide is not fully understood.

The top layer, being the silver sulphide shows a layered structure with cracks running alongside the original surface and perpendicular to it. Inside this layer several cavities and island of metallic silver can be seen (Figure 2). The thickness of the stratified Ag_2S layer varied from 3.7 to 16.3 μm, but typically a thickness of approximately 14 μm was observed. The thickness of the layers that make the stratification varies from approximately 200 – 1250 nm, giving an average amount of 15 relatively thin Ag_2S layers (see also the back scatter images in Figures 2 and 3). It should be noted that a Ag_2S layer thickness of 140 Å (0.014 nm) appears yellow, while a black tarnish layer is approximately 1400 Å (140 nm) thick (Ankersmit, Doménech Carbó et al. in press).The contrast in the back scatter image within the silver sulphide layer is the result of differences in composition and / or density. Unfortunately the composition of the very thin dark grey lines in between the Ag_2S layers could not be analysed by SEM-EDS. The formation of these layers is not fully understood. However, changing environmental conditions might explain this phenomenon.

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[3] Showplate with apotheoses of the arts en sciences, Hans Jakob Mair, 1674, partially gilded silver, Royal Museum for Arts and History, Inv nr. 25 II

www.nma.gov.au

The cracks running perpendicular to the metal surface are most likely caused by brittleness of the Ag_2S layer, combined with differences in crystal orientations and / or shrinkage and volume increase effects related to changing environmental conditions. The cracks running in between the copper sulphide and silver sulphide are most likely the result of differences in crystal packing.

The build up of the overall layers, *i.e.* Ag_2S / CuS / Ag-Cu, differs from what one would expect. Usually, historic silver objects contain a fine silver layer on top of the alloy. This enriched silver layer (approximately 10 µm thick after three times annealing and pickling) is formed by dissolving oxidised copper particles that are formed by annealing the object in vitriol (a diluted H_2SO_4 solution or tartaric acid). Tarnishing will result in a Ag_2S layer on a fine silver layer. In this case apparently all the fine silver has been consumed.

4. Conclusions

Tarnishing of silver is an ongoing process. At first the rate of tarnishing will slowly decrease in time, caused by the diffusion of H_2S that becomes more difficult through a growing tarnish layer. Long exposure of the silver showplate to ambient concentrations of gaseous sulphides resulted in the formation of a thick silver sulphide on top of a copper sulphide layer which is directly bound on the alloy. The Ag_2S layer is stratified. The underlying copper sulphide is heterogeneous. Apparently the overall tarnish layer cannot grow to an infinite thickness. At a certain point the layer flakes from the surface. It breaks in between the silver sulphide and the copper sulphide. The maximum silver sulphide thickness will most likely be determined by the overall presence of silver, *i.e.* the thickness of the original fine silver layer on the object and the alloy composition.

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