THE TIN MERCURY INLAY OF A CABINET MANUFACTURED BY HENDRIK VAN SOEST: A CASE STUDY

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Abstract

The tin inlay of a piece of furniture designed by Hendrik Van Soest has been investigated for its composition, microstructure and corrosion. Small samples were removed and investigated with optical microscopy, micro X-ray fluorescence spectroscopy, scanning electron microscopy with energy dispersive X-ray detection and synchrotron radiation X-ray diffraction. The results show that the inlay is composed of a binary alloy consisting of tin and mercury. The composition suggests the use of an amalgam to produce the metal inlay. However, the microstructure of the inlaid fillets proves that tin sheet was used instead of a tin mercury amalgam.

Corrosion of the tin inlay is the most important sign of deterioration. Analyses show the presence of a thin layer of tin oxide chloride hydroxide in direct contact with the metal. This layer is covered by a layer of the more common tin corrosion compounds romarchite and cassiterite. The harmful effect of chloride containing compound is shown by the advanced corrosion. For future preservation of the tin inlay this compound must be either removed or be immobilized.

Introduction

The tin inlay of a piece of furniture manufactured by Hendrik Van Soest (1659-1716) in Antwerp during the 17th century (collection of the Plantin-Moretus museum, Antwerp, Belgium) shows severe signs of deterioration (Figure 1). The furniture is a typical baroque writing cabinet of oak covered with rosewood veneer. A conservation treatment of the furniture with special attention to the tin inlay is necessary to preserve it. In order to be able to select a suitable conservation method, the corrosion of the metal inlay was studied aiming at the identification of the alloy and the characterisation of its corrosion.

Several publications mention tin to be corrosion resistant. Results have indeed shown that under natural conditions, water and atmospheric oxygen have no harmful effect on metallic tin, although tarnishing of tin is sometimes observed in indoor atmospheric condi-
Nevertheless, tin suffers some corrosion by mineral acids and organic acids in the presence of air. This general idea has in the past led to the belief that tin objects stored under normal museum conditions are little affected by atmospheric corrosion.

Atmospheric corrosion of tin and tin alloys is not well known and understood. As a result tin pest is often considered as the major cause of deterioration of tin objects stored in museums. Tin pest is a physical phenomenon, i.e. an allotropic transformation of metallic white (b-tin) to grey (a-tin) tin which occurs at low temperatures (below 13 °C). Metallic white thin is very ductile while grey tin is brittle. Both forms have a different density (white tin: 7.29 g/cm$^3$; grey tin 5.77 g/cm$^3$) and the conversion results in the transformation of the object into powder. Once an object starts to be harmed by tin pest, it eventually becomes completely destroyed after a period of time and no treatment is effective. Corrosion of tin on the other hand is electrochemical in nature and can be treated in many cases. The most typical and most stable corrosion product of tin is tin(IV)oxide (SnO$_2$).

The general believe that on one hand tin is not affected by corrosion and on the other hand that tin pest is the main degradation form of tin objects, has led to poor conservation practices. As a result today many of the tin objects present in museums are in a certain state of decay. However, detailed examination of several museum objects has shown that they were not affected by tin pest as was first assumed but by tin corrosion. This is also the case for the metal inlay of the cabinet examined here.

Unfortunately, research on the corrosion of tin objects in museums has up to now been relatively limited. In a recent paper results describing the effect of the tin alloy composition and the environment on the corrosion behaviour of tin objects are reported. Nevertheless it remains difficult to develop and improve methods for the preservation of tin objects. In this regard the present work shows that a thorough examination of the corroded tin object is a major aid to a high-quality preservation of the artefact.

2. Experimental

Visual observation of the cabinet gave a first indication about the conservation state of the metal inlay. In a second stage, the composition of the metal was qualitatively determined with an experimental micro X-ray fluorescence spectroscopy setup (microXRF) consisting of a molybdenum cathode X-ray tube, a poly capillary X-ray lens system and a Si(Li) detector.
Three samples of about 2 mm were carefully removed from the metal inlay of the right door pane using a jeweller’s piercing saw. The sampling locations are shown in Figure 2 (a-d). The samples were embedded in resin (Technovit 2000lc) and then ground with silicon carbide grinding papers covering a grain size from 180 mesh/inch to 4000 mesh/inch (Struers) and polished with diamond sprays of decreasing grain sizes, to 0.25 µm (Struers). The embedded samples were viewed using optical microscopy (OM), which allowed us to study the corrosion and microstructure of the samples. Micrographs were taken using a Reichert metallographic microscope MeF3A (Vienna, Austria) for high magnifications and an Olympus LM SZX-12 LM (Hamburg, Germany) research stereo microscope, equipped with a DP 10 digital camera system, for magnifications up to × 90. The composition of the samples and the distribution of elements in the corrosion layer was determined with a JOEL 6300 scanning electron microscope equipped with an energy dispersive X-ray detector (SEM-EDX). In addition synchrotron radiation X-ray diffraction experiments (SR-XRD) were carried out to determine the mineralogical composition of the corrosion. The latter were made at station 9.6 of the Synchrotron Radiation Source (SRS) at Darsebury, UK. An intense monochromatic beam (ca. 100 s collecting time during single-bunch mode and beam current > 20 mA), with high energy (i.e. high penetration) photons (E = 14.25 keV, l = 0.87 Å) and a small beam (100 µm) defined by collimator slits was available. The XRD patterns are collected in transmission by a QUANTUM-4 CCD area detector. Therefore the samples were thin sectioned to about 200-300 µm in thickness. A microscope alignment system allowed the location of the beam on the desired part of the sample. Data analysis was carried out using the ESRF package FIT2D and reference data from the JCPDS PDF cards was used to identify the corrosion compounds.

3. Results and discussion

3.1 Visual appearance

Visual inspection of the inlay work reveals a number of deterioration features (Figure 3): (a) fissures of the tin inlay work, (b) shrinkage fissures in the wood which leads to the release of the metal inlay from the wood, (c) glue bulging out at the edges of the metal, (d-e) black corrosion and (f) yellowish-white corrosion compounds. The black corrosion compounds manifest themselves at small areas and along the borders of the metal inlay. At some places small silvery coloured drops are visible. At locations such as corners, where little wear occurs white-yellow compounds commonly occur. At central areas of larger pieces of metal inlay large grey metallic surfaces, unaffected by corrosion, occur.

3.2 Composition and microstructure

MicroXRF measurements were performed on the metal of one of the panels. The X-ray spectrum (Figure 4) shows the presence of Sn, Hg, Pb and Cu. The Mo signal originates from the used Mo X-ray tube. The presence of mercury in the microXRF data suggests the possible use of tin amalgam to manufacture the metal inlay work. On the other hand, the visual inspection indicates that the edges of the metal inlay do not follow the fine structure of the wood which would be the case if the inlay was manufactured by pressing a fine powdery amalgam into the wood grooves where it receives its metallic appearance. This would indicate ornaments cut out of a metal sheet rather than that a soft tin amalgam, were put into the wood grooves. In what follows we will try to resolve this issue.

SEM-EDX results show that the metal used for the inlay is a tin alloy with mercury and copper as alloying elements (Table 1). It appears that the composition of the three analysed samples varies to a certain extent. In addition sample VSB shows the presence of two phases (VSB phase 1 and phase 2, Table 1). Only two samples VSB and VSC contain a significant concentration of copper as metallic inclusions.

The microstructure (Figure 5b) of the alloy shows signs of working, probably hammering. This

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sn (wt%)</th>
<th>Cu (wt%)</th>
<th>Hg (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VSA</td>
<td>98 ± 1</td>
<td>0.1 ± 0.1</td>
<td>2 ± 1</td>
</tr>
<tr>
<td>VSB</td>
<td>99 ± 1</td>
<td>1.5 ± 0.3</td>
<td>9 ± 2</td>
</tr>
<tr>
<td>VSC</td>
<td>89 ± 1</td>
<td>1.4 ± 0.3</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>VSB phase 1</td>
<td>83 ± 1</td>
<td>1.1 ± 0.3</td>
<td>16 ± 2</td>
</tr>
<tr>
<td>VSB phase 2</td>
<td>96 ± 1</td>
<td>1.8 ± 0.3</td>
<td>2 ± 1</td>
</tr>
</tbody>
</table>

Table 1: Composition (wt%) of the metal inlay and the two phases in sample VSB (RSD for N=3)
enforces the viewpoint that the metal inlay was cut out of a metal plate.

### 3.3 Amalgamation experiments

In the literature only one example where metal inlay is composed of a tin-mercury alloy could be found\(^1\). The author concludes that the tin-mercury inlay alloy of the analysed object is an amalgam pressed into grooves of the wood. No details about the microstructure and the visual appearance of the inlay, however, are reported to support this assumption. The absence of these observations makes comparison between the results and those obtained here impossible.

In order to compare the microstructure of amalgam inlay with the actual inlay studied here, an amalgamation experiment was carried out. A 19\textsuperscript{th} century procedure was followed\(^1\). The different steps of the experiment are illustrated in Figure 6. In this experiment 150 g of tin and 50 g of mercury was melted together in a crucible at 160°C (a). The metal cake (b) was, after cooling, crushed in a mortar obtaining a fine grey powder (c). This powder was put into a groove of a wooden board (d). After pressing the powder into the groove a metallic appearing surface was obtained, which demonstrates that it is possible to obtain metal inlay using a tin-mercury amalgam. However, the microstructure and the elemental distribution of the obtained inlay are different from the samples recovered from the cabinet (Figure 7). Where the inlay of the cabinet shows a grain structure, a more porous structure is observed for the experimental sample. Therefore, it is doubtful that the method described by Stokes was applied to produce the metal fillets studied here.

Another possibility is that the tin plate was polished using a mercury-tin amalgam, similar to the polishing applied to ancient Roman and Chinese bronze mirrors\(^13,14\). Remnants of the mercury could have diffused over time into the tin fillets. An experiment where a small amount of mercury was rubbed over the surface of a tin plate shows that mercury quickly forms a thin layer of amalgam at the surface (Figure 8). However, more extensive research needs to be done to investigate the effect of the presence of a thin layer of amalgam over time on the overall composition of the tin plate. Next to mercury polishing it is possible that mercury gilding or silvering would have been applied. However, no gold or silver is present on the surface which excludes this possibility.

### 3.4 Corrosion structure

In order to characterise the corrosion structure, the surface of the samples was examined with SEM-EDX prior to embedding the samples into resin. The presence of the elements O, Na, Al, Si, Mg, Si, S, Cl, Ca, Fe, Cu and Sn is demonstrated by the X-ray spectra.

Optical micrographs of the cross-section clearly show the presence of a corrosion layer on the surface of the metal. The presence of SnO\(_2\) is indicated by brown coloured compounds (Figures 5b and d). Furthermore, white coloured com-
pounds can be distinguished. The optical micrographs show that the corrosion proceeds on an intragranular way. In addition the corrosion structure is two layered at some locations, where it consists of a well adherent layer and a second amorphous layer. These observations are similar to those of the tin alloys discussed earlier in this chapter.

In Figures 9 and 10, X-ray images of the cross-sections confirm the presence of elements such as Al, Mg, and S at the outer surface of the sample. Furthermore, it appears that the corrosion mainly consists of tin and oxygen which again confirms the presence of tin oxide compounds. At the interface of the metal a thin layer containing chlorine is observed.

To identify the corrosion compounds SR-XRD analyses were performed on thin sections of the sample. Results show the presence of romarchite (SnO), cassiterite (SnO$_2$), Sn$_2$Hg and tin oxide chloride hydroxide (Sn$_3$O(OH)$_2$Cl$_2$ or Sn$_{4+}^{+}$Cl$_{16}$OH$_{14}$O$_6$). Since peak overlap occurs for both minerals of tin oxide chloride hydroxide with other observed compounds, it is difficult, if not impossible, to determine which of the two is present in the corrosion layer (Figure 11).

It appears that the tin fillets are affected by chloride controlled corrosion, resulting in a thin layer of tin oxide chloride hydroxide. This layer is covered by an adherent layer composed of the tin oxides romarchite and cassiterite. At some locations a second loosely adherent layer also composed of tin oxides can be distinguished. The investigations of the small samples indicate that the corrosion structure is similar for both of the surfaces exposed to the air and to the wood. However the situation in the centre of a fillet can be different.

4. Conclusions

The inlay work is composed of a mercury containing tin alloy. The composition indicates the use of a tin mercury amalgam, which is smeared as a powder into grooves carved in the wood thus receiving a metallic appearance. Nevertheless, the presence of cutting marks at the edges and the metallographic structure indicates the use of tin sheet. The dissimilarity of the microstructure and the elemental distribution pattern of the tin fillets from the cabinet with those of an experimentally created amalgam following a 19th century procedure enforces this latter explanation.

Several deterioration signs are observed at the surface of the fillets, corrosion being the most important. The corrosion appears to exist of a thin layer of tin oxide chloride hydroxide in direct contact with the metal. This layer is covered by an adherent layer of romarchite (SnO) and cassiterite (SnO$_2$) and at some locations by a second loosely adherent layer with the same composition.

With regard to the conservation of the metal inlay, the observation of chloride underneath the oxide layer in direct contact with the metal is the most important observation. Oxidation of tin protects the metal for further corrosion. However, because of the presence of a chloride layer contact with the metal the corrosion is not protective here. This means that for a durable preservation of the metal the chloride in the corrosion must be either removed or else be immobilized.
Acknowledgments

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References