Silver

History and Conservation

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Bowl and ewer, Joh. Lutma, 1646
Content

• Vulcan’s workshop
• Authentication and microscopic research
• Current and ongoing research
• Do we know everything of the conservation of silver?
• My questions for you
Vulcan’s workshop

The rolling mill on depictions of Vulcan’s workshop in the 17th century
Vulcans’ forge 1608,
Jan Breughel (the velvet,1568-1625), Ambrosiana, Milaan
Detail
Vulcans’ forge
Jan Breughel (the velvet, 1568-1625)
Vulcans’ forge
Jan Breughel (the velvet, 1568-1625)
Use of the rolling mill in the 16th century

Henry II buys in Augsburg 1551
Rollingmills
Drawbenches
Punch
Mintagepunch
Fasteners for stampholders
Dutch use of the rolling mill in the 17th century
Using horsepower
Perspective drawing
Built up of the rolling mill
The current rolling mill
Example of possible use

Rijksmuseum,
BK-17041-A, Globe, 1709
Augsburg
Thickness = 0,8 mm
Microscopic research

Figure 1. Close-packed hexagonal unit cell structure. Atomic packing factor of 0.74.\(^1\)

Figure 2. Face-centered unit. An FCC structure has four atoms per unit cell and an atomic packing factor of 0.74 in most elemental crystals.

Figure 3. Body-centered cubic unit cell. A BCC metal has two atoms per unit cell and an atomic packing factor of 0.68 in elemental crystals. BCC metals are both ductile and strong (e.g., iron, chromium, tungsten, and molybdenum).
Making the microstructure visible
Grain boundaries
Microstructure of silver
Microstructure of milled silver
Copper coin found on the wreck of the Zuytdorp, 1712
Legacy F.G.S. Baron van Brakell tot den Brakell, 1878
Historic comparison

Hans Jakob Mair, 1674, KMKG Brussel

Unknown, Rijksmuseum Amsterdam
Cross section Ag (ca. 300 µm in total width)
Exfoliation of Silversulphide
A new method for treatment
Exfoliation

Formation of silversulphide

Ag2S

Time
Variable thickness with an average of 14 µm
BSI of silver, copper and sulphur
Combination of Ag, Cu, O and S on the original
Goal for Experiments

• Reproducing the effect where a possible comprehension of the exfoliation takes place.
Reproduction (15x annealed, not worked, 925/1000)

- Enrichment of silver layer
- Thickness pure Ag of 6-8µm
- Enriched Ag/Cu oxidelayer 16-20 µm
EDS-Mapping
925/1000 Ag
15x annealed, not worked
Conclusions

• Tarnished silver exfoliates at an average thickness of 14 µm
• Exfoliation takes place after handling the object
• Coppersulphides and copperoxides stay behind
• Bonded coppercorrosion slows down the tarnishing
• A direct relation between manufacturing technique and tarnishing is evident
Past, Present and Future

De-lamination of mercury gilded silver objects
The Object with surface unclear

History of Technology and History of Art

Materials Science and analytical equipment

Conservation Science and understanding previous treatments

Workmanship and manufacturing techniques

Reproductions showing the effects of the expected decay or original surface

A better understanding of the object with its surface
De-lamination of Mercury Gilded Silver

Mercury gilding and history

- Earliest known use by Chinese 300 BD
- Widely used afterwards in Western Europe (treatises)
- Based on a mixture of mercury and gold on top of a silver alloy
Gold and Mercury

The amalgam is made from pure gold and mercury.
Amalgam is a paste

The mixture is applied on the surface of the object, using brushes, and heated on a charcoal fire.
Drops around the object
Various silver objects with a mercury gilding
Mercury gilding of silver according literature

100% Au
Diffusion zone Au + Ag

Ag/Cu alloy
(925 or 835/000)
Reproduced mercury gilding

500 µm
A mercury gilded silver surface is porous
A tarnished surface as result
Delaminated surfaces
Samples of objects
Materials Science

Crossection and morphology

Even thickness of silver and gold

Channel and island effect
Boundary, between Au/Ag

Kirkendall effect

Porosity behind the boundary
Aim

Reproducing the effect of delaminated mercury gilding
Experiments and reproductions

- Pure gold on silver
- Heating silver alloy at approx 350°C and 700°C
- Reproduction of mercury gilded silver according to a treatise
- Exposing the reproductions to the suspected effects
Reproduction of pure gold on silver without mercury or copper
Diffusion of gold and silver without mercury or copper
(320 °C, 15.5 hrs)
Diffusion of gold in silver at higher temperatures

(660ºC, 15.5 hours)
Comparison of different morphology surfaces
History of Technology and workmanship

Al het zilverwerk dat men wil vergulden moet eerst witgekookt, en schoon gekrest zijn...

Mercury gilding silver according Van Laer’s handbook (1721, 1730 and 1768)

100% Au
Diffusion zone Au + Ag
≈ 100% Ag

Ag/Cu alloy
(925 or 835/000)
Reproduction of silver (15x annealed, not worked, 925/1000)

- Thick pure Ag of 6-8µm
- Enriched Ag/Cu oxidelayer 16-20 µm
- Enrichment of silver layer
Porosity grows due to loss of Ag, Cu oxides do not diffuse into the gold

Ag diffuses in Au

Au does not diffuse back into Ag

Heating 760°C for 2 minutes
Cu oxides present

Pealing off delaminated surface
Reproduction of silver (15x annealed, not worked, 925/1000)

- Enrichment of silver layer
- Thick pure Ag of 6-8µm
- Enriched Ag/Cu oxidelayer 16-20 µm
EDS-Mapping
925/1000 Ag
15x annealed, not worked
SEM images of original and reproduction
Time-Temperature diagram of Ag in Au diffusion
Time-Temperature diagram of Ag in Au diffusion
Conservation Science

• What possible treatments could have taken place in the past that influence the current appearance?
• What possible treatments should take place in order to prevent further loss?
Green corrosion
Recognizing previous treatments
Conclusions

• Heating the mercury gilded silver object after manufacturing will result in loss of material.
• The temperature used for brazing is sufficient for a Kirkendall effect to take place
Further and ongoing research

- Influence of galvanic applied gold layers and possible differences in diffusion
- Which method should be used for cleaning
We know everything of the conservation of silver

Everybody can polish silver..

Everybody can polish silver..
Silver saltcellars
Saltcellar  Claes Claesz Schoon

Amsterdam 1668 (BK-1957-15B)
In detail
Microcracks in the surface

(Magn: 40x)
Conclusion

• Chemical cleaning will cause problems
• Microscopic research with every object before treatment
Conservation of historic silver

• The object is in a showcase
• The object will be exhibited outside a showcase
• The object is in storage

Rijksmuseum, 1927
Silver on display

• The showcase should be closed and contain no materials which can give off S (given tests are the Azide test and the accelerated aging test)

• If the showcase has an opening of 1 mm² the exchange rate will be ...... thus the outside environment will be exchanged x times a day

• The showcase should be made of safety glass (which can have its disadvantages as well)
Disadvantages of safetyglass

(no outside reflection was allowed to take place)
Silver objects outside a showcase

The possibilities for conservation are:

Doing nothing

- Advantage: beautiful lustre if the $\text{H}_2\text{S}$ concentration is low
- Disadvantage: $\text{H}_2\text{S}$ concentrations are never that low, meaning cleaning many times and therefore loss of material
- Conclusion: it is better to lacquer the object

Lacquering the object with three possible methods, *dipping*, *brushing*, and *spraying*. The lacquer which is most suitable is a nitrocellulose lacquer, ercalene or frigilene

How do we remove the lacquer?
Dipping a lacquer

Until 1995 all silver objects in the Rijksmuseum were dipped in frigilene (nitrocellulose lacquer).

• Advantage: the whole object is covered with lacquer
• Disadvantage: crevices are filled with lacquer which become hard to remove. An iridescent curtain effect is in many cases the result. Because of slow evaporation of the solvent; dripping is visible.
• Conclusion: the layer of lacquer is too thick, therefore the iridescence is disturbing
Iridescent curtain effect
A lacquered object
Brushing the lacquer

Various museums around the world brush lacquer their objects

• Advantage: a fume hood is enough for safety

• Disadvantage: if one spot is missed, accelerated corrosion will take place, turning part of the object specifically black

• Conclusion: it is better to spray lacquer
Accelerated tarnishing
Spray lacquering the object

All silver objects in the National Maritime Museum, London are spray lacquered with frigilene.

- Advantage: the chances for obtaining a better covering are much larger, no brushstrokes are visible
- Disadvantages: practice is needed to do it properly and a special fume exhaust is needed.
- Conclusion: the best way to lacquer your silver, there are always companies who can do this for you
Conservation of silver at the Rijksmuseum

- 1240 objects on display
- 2117 objects in storage
Keep it from tarnishing

- [C]
- $\text{H}_2\text{S}$ emission
- Foil
- Distance
The costs

• ArchiPress Pouches 100 pieces (27 x 41cm) 90,53 euro
• ArchiPress Pouches 100 pieces (28 x 50 cm) 155,83 euro
• Sealdevice 1.430,- euro
Labour

• 5 minutes at 28 hours is approx. 7 weeks.

• But 2 minutes at 28 hours is approx. 3 weeks
Result
New showcases
And than cleaned..