Solder on silver: historical usage and the problem of fretting

M.J.T.M. van Bellegem[a], H.A. Ankersmit[b], R. van Langh[c] and W. Wei[d]

[a] Westerstraat 242-II, NL-1015 MT Amsterdam, The Netherlands,
[b, d] Netherlands Institute for Cultural Heritage, P.O. Box 76709, NL-1070 KA Amsterdam, The Netherlands.
[c] Rijksmuseum Amsterdam, P.O. Box 74888, NL-1070 DN Amsterdam, The Netherlands.

Abstract

A preliminary study is being conducted in order to determine the cause of fretting of silver objects by tin-based solders. The microstructures of reproductions of historic solder joints as well as model samples are being examined using optical and scanning electron microscopy (SEM). Thus far, it has been found that soldering, which generally occurs at approximately 200 °C, appears to result in the formation of an Ag_3Sn layer as a result of the dissolution of silver by tin. Above 221 °C, the Ag_3Sn layer goes partially into solution and is in equilibrium with a Sn rich liquid phase. Thus, typical methods to remove solder by reheating above the soldering temperature only partially remove the Ag_3Sn layer and allow free tin to further dissolve silver. This dissolution is slow enough that it is not obvious to the naked eye. During the restoration of a soldered joint by brazing, temperatures rise above 480 °C. At these temperatures, the Ag_3Sn layer has completely decomposed. Free tin dissolves silver, but now at a much higher rate, resulting in fretting. In order to avoid fretting, it is thus important to find a method to remove the Ag_3Sn layer before brazing.

Keywords: (soft) solder, brazing, silver, tin, lead, fretting, intermetallic compounds

1. Introduction

Silverware, which has been repaired using soft solders, based on alloys of tin (Sn) and lead (Pb) poses several problems to conservators. The solder has often been applied extensively, thus disturbing the surface and the colour of the object. The solder joints are often weak in comparison to joints executed with silver brazes, and are thus more prone to failure. It should be taken into account that the desired strength for a repair depends the function of the object. The solder may also be the cause of a form of damage to the silver object known as fretting (Brehpohl 1996; Untracht 1975; Urs Stussi 1988; Cuzner 1965; Wylie Davidson 1913). Fretting is a term used to indicate the damage caused by the dissolution of silver by tin-lead solders, the silver being "eaten away" as it were. Fretting appears as dark spongy spots in the silver surface, (see for example, Figure 4 in Niemeyer,1997, p191). Replacing the soldered joint with silver brazing often results in failure due to fretting.

Corresponding author: TEL: +31204704746, metalsconservation@yahoo.com

The conservator or silversmith thus has several options for repairing soldered joints:

1. Reapplication of solder.
2. Removal of solder using mechanical or chemical methods, followed by brazing.
3. Removal of solder using mechanical or chemical methods, followed by gluing.
4. Removal of the affected area of silver and replacement with a new piece of silver.

Currently, conservators and many silversmiths find the use of solder on silver unnecessary and undesirable (conservators also find brazing to be undesirable). Gluing is a possibility (often used with fiber reinforcement), and is generally the preferred alternative (Costa 2001). However, gluing (third option above), as well as reapplication of solder (first option), have the disadvantage that the resulting joint is still weak. This can be a problem in cultural collections where objects may still have a functional use. However, for objects in a museum collection, the demands on usage are different and choices will often be made in favor of a weaker joint so that it will fail preferentially in order to avoid damaging the original parts of the object. The fourth option, replacing the affected area of silver, is more complex and is fraught with ethical issues. The second option is thought to provide a stronger joint and to result in the least amount of damage to the silver object, though in most cases. However, the phenomenon of fretting when brazing former solder joints is well-known by gold- and silversmiths and has prevented brazing from being more widely accepted.

It is not clear from the literature whether fretting is caused during soldering, or later, for example during removal of the solder and subsequent brazing. A microstructural study is thus being conducted to determine the cause of fretting and to find solutions for avoiding the problem.

2. Experimental procedure

Microstructural studies are being conducted on reproductions of historical solder joints, and on model solder samples where soldering conditions are systematically varied. To study the soldering process and the influence of various parameters on the interaction between solder and silver alloy during soldering, a series of reproductions have been carried out. 925/000 (sterling) silver discs (Degussa), 5 mm diameter and 1 mm thick were soldered in the centre of 30 x 30 x 1 mm 925/000 silver sheet (Degussa) specimens using a propane/oxygen gas torch. Various combinations of fluxes and solders as found in historical sources were used, see Table 1.

Table 1

Solder / Flux combinations used in historic reproductions
(compositions in wt.%)

Solder	Flux
50Sn-50Pb	S-39 flux (containing ZnCl)
50Sn-50Pb	one of the following: • tallow • colophonium
60Sn-40Pb	S-39 flux (containing ZnCl)
96.5Ag-3.5Sn	flux for Sn-Ag solder (Felder GmbH, containing zinc chloride, ammonium chloride, hydrochloric acid, isopropanol and water)

Before soldering, the surfaces were polished with 800 grit paper and then cleaned with ethanol. Soldering was conducted using a propane/oxygen torch. The temperature of the backside of the silver sheet (away from the solder) was measured with a thermocouple (Testo 925™). After soldering, the specimens were cooled in air and the flux remnants were rinsed off with tap water.

The repair of a solder joint by brazing was also simulated. The solder was removed from the 50Sn-50Pb specimen by melting, shaking as much solder as possible off, and wiping the rest off with a cloth. The silver disc was then reattached using a soft silver braze with borax as the flux.

Based on the results of the reproductions, the interaction of soldering materials with silver was studied. 50Sn-50Pb solder, pure Sn, or pure Pb were melted and held at various temperatures on 925/000 silver or pure silver sheet specimens cast from fine silver granules (Degussa; 30 x 30 x 1 mm), see Table 2. The experiments were conducted in a Carbolite™ oven. After heating for the specified time, the specimens were cooled in air.

Table 2

Test parameters for investigation of interaction between solder materials and silver
(compositions in wt.%)

- 50Sn-50Pb on 925/000 silver sheet specimens, held for 4 minutes at 200, 400, 600 or 800 °C
- Pure Sn on fine silver sheet specimens held for 4 minutes at 400, 600 and 800 °C
- Pure Pb on fine silver sheet specimens held for 4 minutes at 400, 600 and 800 °C

Cross sections were cut from the soldered specimens and prepared metallographically using techniques recommended by Struers. The sections were embedded in Specifix Resin, ground using Hermes waterproof paper (220, 800, 1600 and 3200 grit) polished with nine, three, and 1 μm diamond spray using DP-Lubricant blue, green and red on MD-Largo and MD-mol polishing cloths. For this initial work, results are given for the unetched condition. The microstructure of the reproduction solder joints, and the interaction zones between soldering materials and silver were examined using a JEOL- JSM 5910-LV scanning electron microscope (SEM) with a

Vantage Termonoram energy dispersive spectroscopy (EDS) system at high vacuum and 20 kV accelerating voltage. Line scans were made across the solder/silver interfaces to investigate the diffusion of the various elements between the solder alloy and the silver substrate. Elemental mapping and analyses were conducted using EDS to determine phase relationships in the microstructure. Any loss of silver due to fretting or other attack was measured as the loss in thickness of the silver sheet.

3. Results

Typical temperature-time curves for the various soldered joint reproductions are shown in Figure 1 for 50Sn-50Pb solder using S-39 flux, tallow, or colophonium as flux. All of the other tested soldering processes showed similar temperature behavior. The maximum temperature was reached within 15 seconds, and cooling in air took up to five minutes. This behavior would be expected for hand soldering, where the part would be heated only until the moment that the solder melted and flowed. It should be noted that the measured temperatures, especially the maximum around 200 °C, are probably lower than the actual temperatures, since the thermocouple was placed on the reverse side of the silver sheet, away from the soldering process.

The loss in thickness of the silver sheet in selected samples is given in Table 3. In spite of the reaction of Sn with Ag, it can be seen that the soldering process results in only a small loss in thickness of 16 µm for the 50Sn-50Pb (nr. 1 in Table 3). This value falls within the uncertainty of the measurement of the thickness of the unsoldered sheet material. A 96.5Sn-3.5 Ag solder tested in this programme also showed a similar loss in thickness (nr. 2 in Table 3). Removal of the solder by remelting, removal of the disc, shaking, and wiping resulted in further loss of silver to a total of about 50 µm (nr. 1a). Brazing the disc back onto the silver sheet increased the total loss to over 90 µm, in spite of the fact that no additional Sn-Pb solder was used. The temperature during brazing reached over 480 °C, and remained above the temperature for soldering (around 200 °C) for almost two minutes. At higher temperatures the reactivity of Sn can be seen by the large thickness losses for specimen nrs. 4 and 5 in the table. Pb on the other hand, does not show a reaction layer with Ag even at 400 °C. The small thickness loss value shown, (nr. 3) is also within the uncertainty of the measurement of the original thickness of the Ag sheet.

Table 3

Loss in thickness of silver sheet after soldering

Nr.	Sample	Loss of thickness (µm)
1	Ag disc soldered onto Ag sheet using 50Sn-50Pb solder with S-39 flux	16
1a	Ag disc soldered onto Ag sheet using 50Sn-50Pb solder with S-39 flux; removal of the solder	50
1b	Ag disc soldered onto Ag sheet using 50Sn-50Pb solder with S-39 flux; removal of the solder; brazed	92
2	Ag disc soldered onto Ag sheet using 96.5Sn-3.5 Ag solder with S-39 flux	19
3	Pb on Ag held for 4 min. at 400° C	12
4	Sn on Ag held for 4 min. at 400° C	101
5	Sn on Ag held for 4 min. at 800° C	439

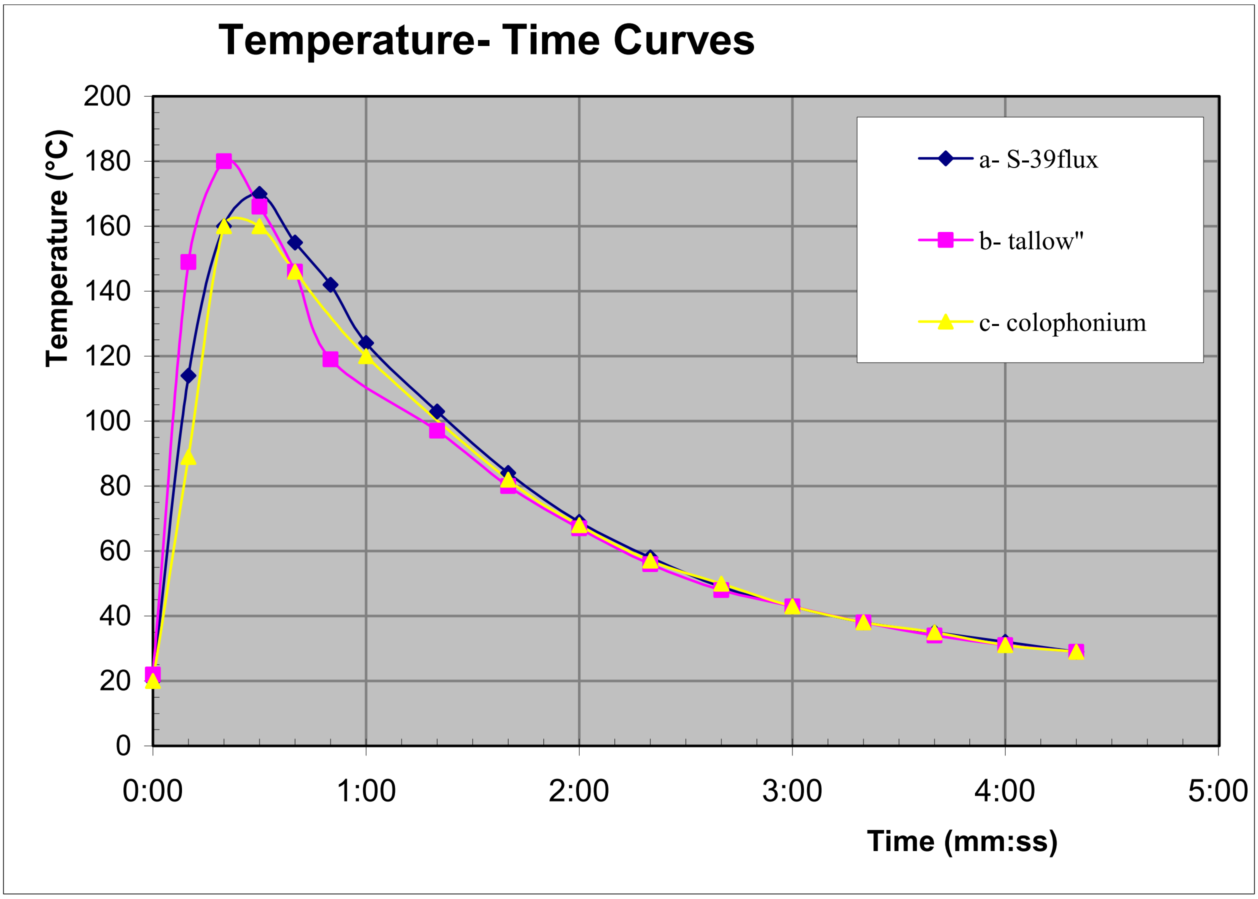


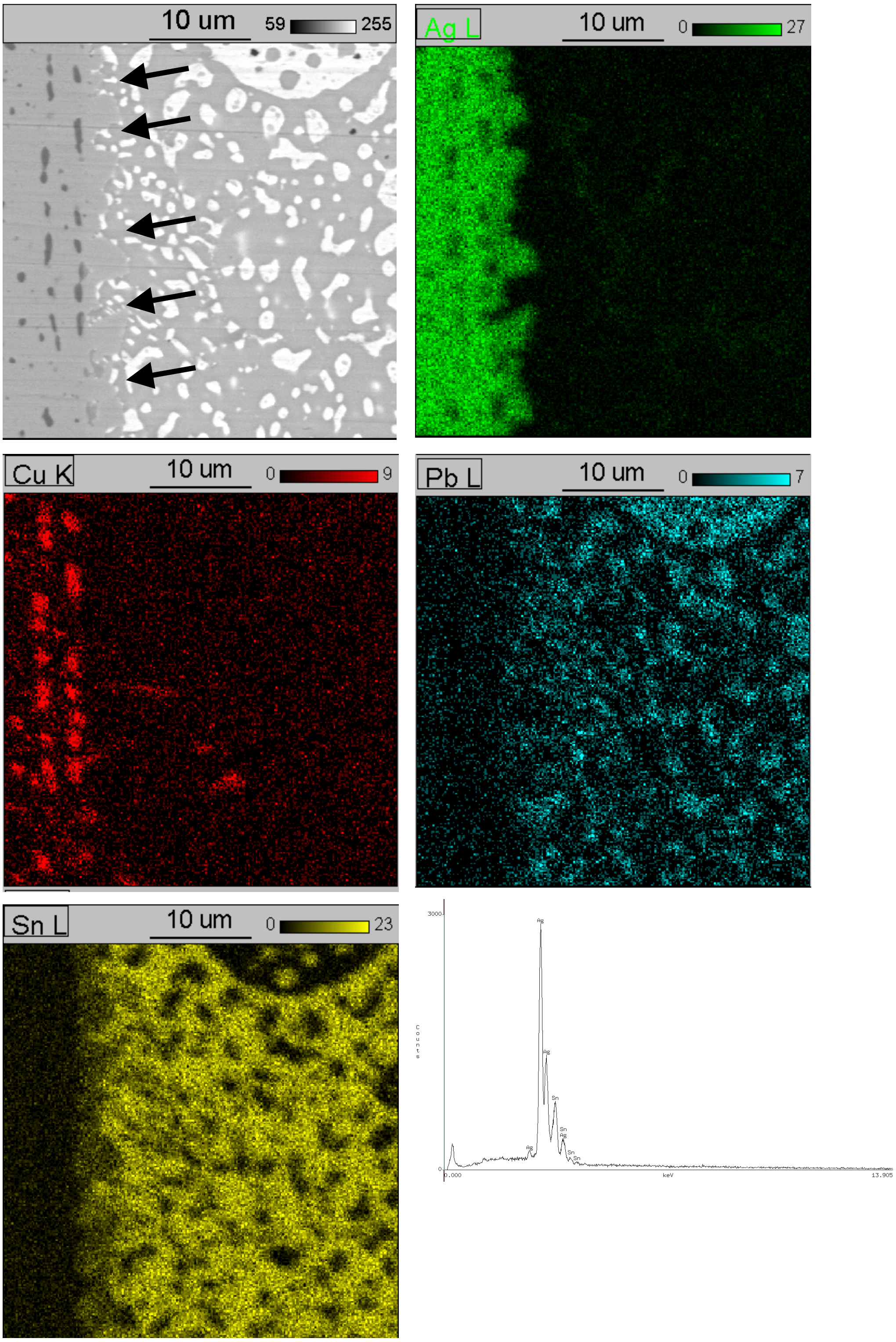
Figure 1 - Typical temperature-time curves during the soldering process with 50Sn-50Pb solder using the following fluxes:

a) S-39 flux
b) tallow
c) colophonium

An SEM-micrograph of soldered joint reproduction using 60Sn-40Pb solder and 925/1000 silver is shown in Figure 2 along with corresponding elemental maps for Ag, Cu, Pb and Sn. To the left, one can see the silver sheet with a dark elongated Cu-rich phase, typical for rolled material. To the right, the eutectic structure typical for Sn-Pb solders can be seen, where the white phase is Pb-rich phase.

The interface in the centre of the micrograph has an irregular finger-like structure, see arrows in Figure 2. The fingers have a length of 2-3 μm. The elemental maps, Figs. 3bcde show that Ag and Sn overlap in this region, with the overlap corresponding exactly to the finger-like structure. EDS analyses, Figure 2f and line scans of these fingers show a chemical composition of approximately 75 wt.% Ag, 25% wt. Sn. This corresponds to the composition of the intermetallic phase, Ag_3Sn, often found in electronic solder joints (see for example, Humpston 1993, Unsworth and Mackay 1973, Bulwith and Mackay 1985). The interface of 50Sn-50Pb specimen had a similar appearance.

In Figure 3, a 50Sn-50Pb specimen is shown after trying to remove the solder. Figure 3a shows that there is still a layer of material attached to the silver sheet. Elemental mapping, Figures 3bc and EDS analysis show that this is again a mixture of Ag and Sn in the ratio expected for the Ag_3Sn intermetallic phase. Traces of Cu and Pb are also to be found in the outer surface of this layer. This possibly indicates that Cu has also reacted with Sn, and that some solder (as evidenced by the Pb) remains on the surface.



a b c d e f

Figure 2 - SEM micrograph and elemental maps for a specimen soldered with 60Sn-40Pb and S-39 flux.
a)-SEM micrograph- arrow shows finger structure described in text
b)- Ag map
c)- Cu map
d)-Pb map
e)- Sn map
f) EDS spectrum from one of the fingers (arrow)

a b c d e

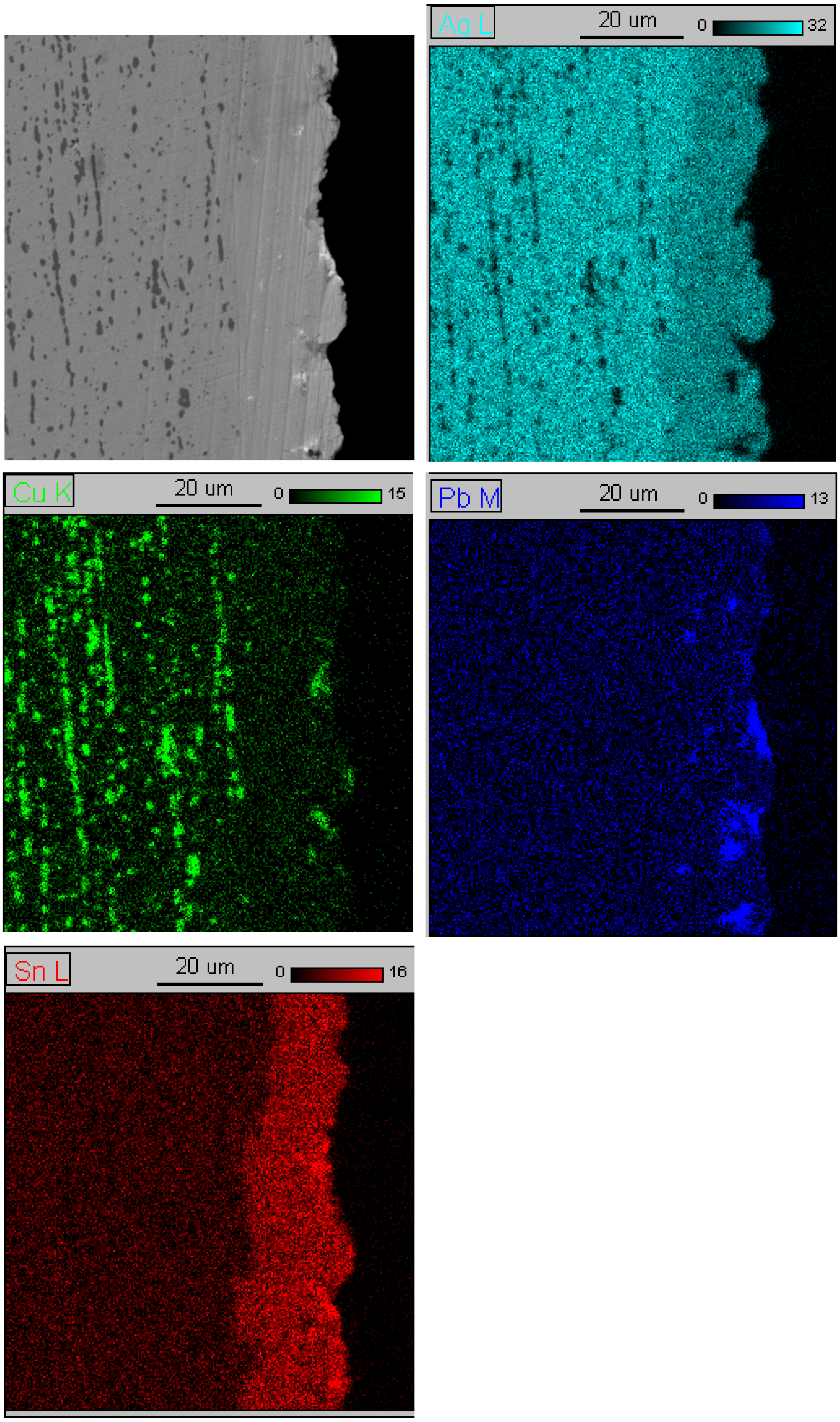


Figure 3 - SEM micrograph and elemental maps for a specimen soldered with 50Sn-50Pb solder, where the solder was then "removed" by remelting, shaking and wiping.
a) SEM micrograph
b) Ag map
c) Cu map
d) Pb map
e) Sn map

4. Discussion

The initial results of this study show that historical methods of soldering silver objects result in the reaction of Sn with Ag, creating a thin reaction layer most likely consisting of the intermetallic phase, Ag_3Sn. Removal of the solder by remelting, shaking, and wiping does not appear to be successful, as the intermetallic layer remains, Figure 3a. In addition, there is a slight additional attack of the silver by Sn. Brazing on top of the remaining solder causes further attack, with the thickness loss being almost the same as for the combined processes of soldering and cleaning. This additional attack would be the fretting attack commonly experienced by conservators.

The explanation for the further attack of Sn, in spite of the fact that no additional solder is used in brazing, and obviously when removing the original solder, can be found by considering the equilibrium phase diagram for the Ag-Sn system, see Figure 4.

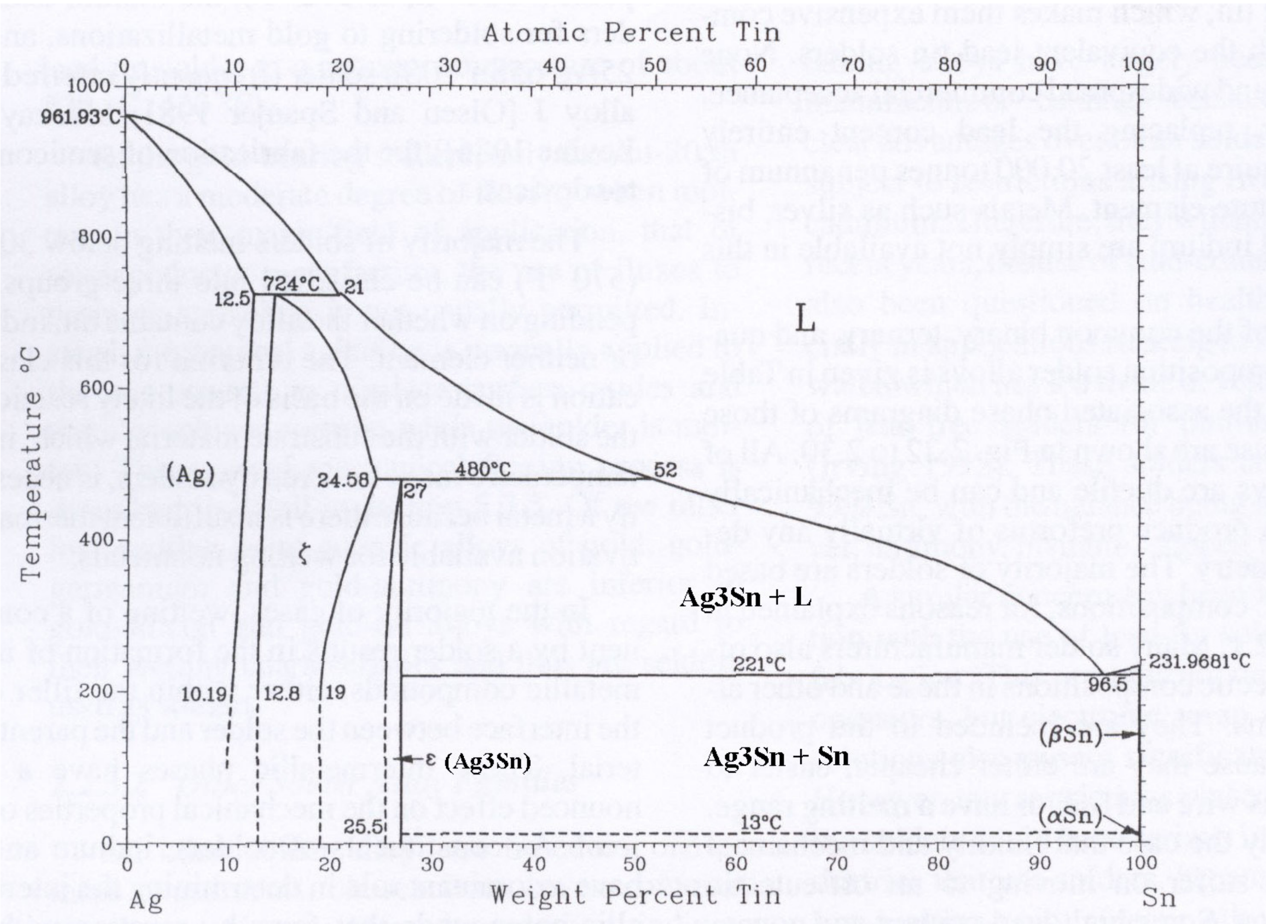


Figure 4 - The Ag-Sn equilibrium phase diagram. Adapted from Humpston 1993, p.78

During soldering by hand, temperatures can rise above 200 °C, resulting in a two-phase equilibrium between Ag_3Sn and a Sn rich liquid. This Sn liquid phase will dissolve Ag. Upon solidifying, the intermetallic phase Ag_3Sn will form as part of the reaction layer. However, the equilibrium diagram shows that below 221° C, a eutectic mixture of Ag_3Sn and a Sn-rich phase are to be expected. An equilibrium phase diagram cannot be used to describe a dynamic process such as cooling, but given that solder joints are generally cooled in still air, there may be enough time for some of the Sn-rich phase to form.

When traditional methods are used to remove the solder, the joint is probably heated to temperatures similar to those used for soldering, around or above 200 °C. This will be sufficient to melt any unreacted solder lying above the reaction zone. However, the eutectic temperature for Ag-Sn is 221 °C. The Ag_3Sn - Sn eutectic microstructure most likely remains in the solid state. If the temperature should rise above 221 °C, only a small amount of the eutectic will melt, and that would initially be the Sn-rich phase. Thus the Ag_3Sn layer remains on the surface and the Sn-rich phase is free to react with the Ag.

When brazing silver, much higher temperatures are used, well above 450 °C (which is the generally accepted difference between soldering (< 450 °C) and brazing (> 450 °C) (Humpston 1993)). At those temperatures, much of the Ag_3Sn will have melted, again releasing Sn into the liquid phase. Thus the solder, which was not removed, that is, that in the reactive layer, is again aggressive. However, the temperatures are now much higher than for soldering.

The model specimens show that the reaction of Sn with Ag is much higher at higher temperatures, 400 ° and 800 °C This agrees qualitatively with the literature, which shows that the solubility of Ag in Sn increases with temperature according to an Arrhenius relationship (see Bader 1969, Unsworth and Mackay 1973, Bulwith 1985, Klein Wassink 1989 and Humpston 1993). Pb does not appear to attack Ag, at least at 400 °C (merely 12 µm of penetration, see table 3 nr.3). Thus, the Sn remaining on the material under the braze will be highly reactive, and "fretting" will occur.

The origins of the problem of "fretting" of silver objects by solder can be understood by looking briefly at the history of the soldering and brazing of silver. The historical development of soldering and brazing techniques has been reviewed, among others, by Allen 1978, 1984; Wolters 1983ab and Schmidt 1993. The Greeks and Romans are known to have used tin-lead alloys for soldering (Allen 1978). Schmidt (1993) mentions that tin-lead alloys and pure tin were used on silver, in particular, objects of the Hildesheimer Silberfund. Wolters (1983) discusses the use of brazes on silver, including a silver-tin alloy described in the *Mappae Clavicule* (ca. 825 A.D.) with a liquidus of 937 °C and silver-copper-tin alloys used in the Middle Ages.

In the late medieval period, brazing became more important. This can be seen in guild specifications for the amount of noble metals to be used in brazes (Weber 1959, p.65; Fock 1983, p.42). It is known that silver objects had to be assayed for the amount of silver used in the alloy. Silver objects were often a way of investing money. When necessary they could be melted down and made into coins. This was more difficult if solder had been used on an object. Impurities of lead or tin in gold or silver alloys could lead to a brittle alloy (Wolters 1981, p.49 and 63; Brehpohl 1996, p.303) and present problems when working with these alloys. The use of solder on silver would therefore be undesirable.

The 18th century provides more documentation about soldering and brazing techniques. The treatise of the Dutch silversmith, Willem van Laer (1674-1722) does not mention the use of solders on silver (see reprint, Laer 1967). However, Laer does mention a 'soldeer-lamp', which he designed for use on small failures or holes in joints. The advantage of that lamp was that the work did not need to be placed into the full flame of a coal fire with the risk of melting previous joints. The work was heated in the coal fire until it glowed, then was taken out of the fire, and locally joined by directing the flame with a blowpipe. Based on that description, the lamp was probably used for brazing with silver brazes. In 1760, Johann Georg Friedrich Klein described the use of a 'Lóthlampe' (lóth = soldering/ brazing) (see reprint, Klein 1987). The lamp was mounted on a wooden box with little drawers used to hold 'Schlagloth, Borax und anderes kleines Lóthgeráthe' (brazes, borax and other small soldering tools). This indicates that this type of lamp was used for brazing, since borax is a flux used for brazing. Klein also describes other methods for soldering, including

- casting on parts by pewterers
- the use of a soldering bit by tinkers
- use of thin wires of solder and a blowpipe for directing a flame, used mainly by pewterers, possibly derived from techniques used by gold- and silversmiths
- use of colophonium to help solder flow on an object placed in a coal fire, used mainly by coppersmiths
- heating small objects on top of small iron-melting furnaces, used by 'Zinnknopfmachern' (tin button makers).

Further improvements in the method of heating the work came in the 19th century with the invention of the gas burner by Bunsen (Fock 1983) and the development of the electric soldering bit.

Literature from the twentieth century presents different views about soldering. Some sources claim that it can be used for all metals (Cuzner 1965; Diebener's Handbuch 1936). Others say it should be used only as a last resort on gold or silver (Untracht 1975, Fachkunde Edelmetallgewerbe 1981, Brehpohl 1969, Urs Stussi 1988, Braun-Feldweg 1968, Wylie Davidson 1913) or that it should not be used on gold or silverware at all (Finegold 1983, Staton Abbey 1968, Weber 1959). In general it can be said that the use of solder during the manufacture of historical silver objects is limited, which means that the presence of solder on historical silver objects is generally due to repairs.

From this brief review of the soldering and brazing of silver, it is clear that in conservation, this work is performed by hand with no accurate means for temperature control, that being not only which temperature, but also time at temperature. The application of solder on silver could have been done by either conservators or gold- or silversmiths who saw no other possibility than using solder, or by untrained workers. The results of the current research programme indicate that it is virtually impossible to remove solder from a silver object using traditional methods. Any attempt to resolder, clean, and/or braze will release some, if not, all of the tin bound in the reactive layer, allowing it to further attack the silver. This can occur at any temperature above the eutectic temperature for Ag_3Sn - Sn, 221 °C, but is more rapid at the high temperatures used in brazing. However, the fact that there is a range of temperatures where fretting is observed, could be a cause for the confusion in the literature and in seemingly conflicting anecdotal stories about fretting.

The best solution to the problem of fretting is, in any case, to find a method for removing all remnants of solder, including the Ag_3Sn reaction layer. These could include a combination of mechanical and/or chemical techniques. However, they will all require knowledge of how deep the solder has attacked the silver. There will also be a number of important practical and ethical issues associated with possible solutions.

5. Conclusions

An experimental study has been conducted to determine the cause of fretting of silver during the restoration of solder joints by brazing. Microstructural analysis was performed on historical reproductions of soldered joints, joints repaired by brazing, and samples modelling the soldering and brazing processes. The results indicate that the original soldering process itself does not lead to fretting. However, there is limited dissolution of silver by tin from the solder, which results in the formation of an Ag_3Sn layer at the interface between the solder material and the silver object. At temperatures above 221 °C, that is, just above the soldering temperature, this Ag_3Sn layer goes partly into solution, creating a two-phase equilibrium of solid Ag_3Sn and a Sn-rich liquid. Thus, the solder and reaction layer cannot be removed by merely melting and removing it mechanically. This Sn-rich phase can attack the silver object further. At temperatures common for brazing (well above 400 °C), this dissolution process occurs at a much faster rate, resulting in the visually apparent problem of fretting. Mechanical and or chemical methods must be developed to completely remove this Ag_3Sn layer before brazing in order to avoid fretting.

Acknowledgements

This paper is the result of a thesis project conducted by the first author for a diploma in conservation at the Netherlands Institute for Cultural Heritage (ICN), Amsterdam. He would like to thank the Rijksmuseum Amsterdam for providing the facilities for the work. In addition he would like to extend his appreciation to Ineke Joosten (ICN) for assistance with the SEM work, P. Hallebeek (ICN) for x-ray analyses, and Ilonne de Groot, Ink de Pree, and Loes Siedenburg (all ICN), Russell Wanhill (Netherlands Laboratory for Aerospace Research), Antoinette Verhage, and Camiel Aalberts for their assistance and helpful discussions.

References

Allen, B. M. (1978) *Discovering soft-soldering history,*. The Metallurgist and Materials Technologist, October 1978, (London) p.537-540.

Allen, B.M. (1984) *Bibliography of books on soft soldering (1760-1983),* In: Klein Wassink, R.J. (ed.). Soldering in Electronics, (Ayr: Electrochemical Publications Limited) p.454-458

Bader, W.G. (1969) *Dissolution of Au, Ag, Pd, Pt, Cu and Ni in a molten tin-lead solder*. Tests indicate that palladium, copper, silver and gold are unsuitable for thin-film applications if they are to serve as substrate films for 60Sn-40Pb solder'. Welding Journal; Welding Research Supplement, Vol. 48, p.551-557s.

Brehpohl, E. (1996) *Theorie und Praxis des Goldschmieds* (Leipzig: Fachbuchverlag)

Braun Feldweg, W.(1968) *Metal, Werkformen und Arbeitsweisen* (Ravensburger: Otto Maier Verlag)

Bulwith, R.A. and Mackay, C.A. (1985) *Silver scavenging inhibition of some silver loaded solders*. The results of experiments show that silver dissolved in a solder alloy has an inhibiting effect on the scavenging of silver from silver substrate'. Welding Journal; Welding Research Supplement, March 1985, p.86-90s.

Costa, V. (2001) *The deterioration of silver alloys and some aspects of their conservation,* Reviews in Conservation, number 2, (London), p.18-34.

Cuzner, B. (1965) *A Silversmith's Manual, treating of the designing and making of the simpler pieces of* domestic *silverware*, (London: N.A.G. Press, Ltd).

Diebeners Handbuch Des Goldschmieds, ein werkstattbuch fur die Praxis, (1936). (Leipzig: Verlag von Wilhelm Diebener)

Finegold, R. and Seitz, W.(1983) *Silver smithing*, (Radnor:Chilton Book Company)

Fock, W (1983) *Technieken in de kunstnijverheid, 1 goud en zilver*, (Leiden: Kunsthistorisch instituut, Rijksuniversiteit Leiden)

Humpston, G. and J, David M. (1993) *Principles of Soldering and Brazing,* (Ohio: ASM International)

Klein, J.G. F. (1987) *Ausführliche Beschreibung der Metalllothe und Lothungen, darin sowol alle Schlag- Schnell- Hart- Weich- Metall- und andere lothe zu machen; als auch alle Metalle selbst zu lŏthen, angewiesen werden von Johann Georg Friedrich Klein, im Verlag des Buchladens der Realschule, Berlin 1760*, (Leipzig: Deutscher Verlag fur Schweisstechnik Gmbh).

Laer, W. van. (1967) *Weg-wyzer voor aankomende goud en zilversmeden*, (Lochem: De Tijdstroom)

Niemeyer, B. (1997) *Early 20th-century restorations and modern conservation treatments on archaeological silver objects*'. Metal 95, Proceedings of the international conference on metals conservation, (London: James & James) p.190-195.

Schmidt, H. (1993) *Übersicht zur wissenschaftlichen Literatur über das "Löten und Schweißen in der Antike/ Altertum*'. Berliner Beiträge zur Archäometrie, 12, (Mainz) p.5-53.

Staton Abbey, (1968) *The Goldsmith's and silversmith's handbook, a practical manual for all workers in gold, silver, platinum and palladium, based on the well-known handbooks by George E. Gee*, (London: The technical press Ltd.)

Unsworth, D.A., and Mackay, C.A. (1973) *A Preliminary Report on Growth of Compound Layers on Various Metal Bases Plated with Tin and its Alloys,* Transactions of the Institute of Metal Finishing, Vol 51, (London) p.85-90.

Untracht, O. (1975) *Metal Techniques for Craftsmen*, A basic manual for craftsmen on the methods of forming and decorating metals, (London: Robert Hale Limited)

Urs Stussi, F. (1988) *Schmuck, Material, Design, Herstellung*, (Ravensburger: Ravensburger Buchverlag Otto Maier GmbH)

Weber, A. (1959) *The Jeweler, directives and targets to be attained in training apprentices*, (Geneva: Office for Industrial Information, Hugo Buchser(translated from german in 1955)

Wolters, J. (1981) *Der Gold- und Silberschmied, Band 1, Werkstoffe und Materialien*, 1.Auflage (Stuttgart: Ruhle-Diebener-verlag GmbH & Co.KG)

Wolters, J. (1983a) *Zur Geschichte der Lötung von Edelmetallen, Teil 1: Historische Entwicklung der Lotlegierungen,* Zeitschrift für Archäometrie 1/2. p.48-64

Wolters, J. (1983b) *Zur Geschichte der Lötung von Edelmetallen, Teil 1: Historische Entwicklung der Lotlegierungen*, Zeitschrift für Archäometrie 1/3. p.86-98

Wylie Davidson, P. (1913) *Educational Metalcraft, A practical treatise on repousse, fine chasing, silversmithing, jewellery, and enamelling, specially adapted to meet the requirements of the instructor, the student, the craftsman and the apprentice*, (London, New York, Bombay, and Calcutta: Longman's Green, and co.)